STRUCTURE AND PROPERTY CONTROL IN SEMICRYSTALLINE POLYMERS THROUGH BLOCK COPOLYMERIZATION, MACROMOLECULAR ARCHITECTURE, AND TACTICITY

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Abstract

This dissertation presents three examples of how the structure and properties of semicrystalline polymers can be controlled through careful design of key aspects of the polymer chain. Linear and 6-arm star block copolymer thermoplastic elastomers (TPEs) comprising crystalline, glassy, and rubbery blocks are prepared by anionic polymerization, chlorosilane coupling, and hydrogenation optimized for the preparation of well-defined structures. Two pentablock copolymers, with the block sequence crystalline-glassy-rubbery-glassy-crystalline, are evaluated and compared against triblocks with either crystalline or glassy end blocks. Judicious choices of block lengths yield disordered melts for both pentablocks, dramatically improving the processability compared to the more conventional microphase-separated glassy-rubbery-glassy triblock.

In the pentablocks, crystallization of the end blocks followed by aggregation and vitrification of the glassy blocks produces composite crystalline-glassy physical cross-links. The pentablocks are elastomeric with lower Young’s moduli and higher ultimate strengths than the crystalline-rubbery-crystalline triblock—both desirable qualities for a soft TPE—highlighting the strong influence of the crystal morphology on the mechanical performance. Compared to their linear counterparts, 6-arm star TPEs with the same block motifs exhibit similar phase behavior and equivalent or improved ultimate strength, recovery, and hysteresis. The covalent junction at the core of the star strengthens and accelerates the recovery of the network, but does not prevent plastic deformation of the crystallites.
At the other extreme, strongly segregated crystalline-rubbery diblock copolymers, in which crystallization is confined by the melt morphology, are investigated. Confined crystallites are forced to adopt a texture where the $b$-axis lies in the plane of the microdomains and the $c$-axis is tilted with respect to the lamellar normals; the tilt angle increases with increasing molecular weight. The lamellar spacing dilates substantially (by 15–30%) upon crystallization, but the maximum crystal thickness is limited by the rubbery domains.

Finally, tactic hydrogenated polynorbornenes (hPN) are examined. hPN is unique in that the isotactic ($i$), syndiotactic ($s$), and atactic ($a$) forms are all semicrystalline with distinct crystal structures. Additionally, $ih$PN shows evidence of polymorphism. Estimates of the $c$-axis dimensions of $ih$PN and $sh$PN suggest slightly kinked chain conformations. The melting points of $ih$PN and $sh$PN bracket that of $ah$PN.
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In a sense, this section has taken the longest to write. I am indebted to a great many people, and these few pages will surely be insufficient to express my gratitude. I must first acknowledge the funding and collaborations which made this work possible. Primary support was provided by the National Science Foundation Polymers Program (DMR-1003942 and DMR-1402180). I am grateful to Dr. Andrew Bell (Promerus, LLC) and Prof. Richard Schrock and his group (Massachusetts Institute of Technology) for providing some of the materials for Chapters 7 and 8.

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Chapter 1

Introduction

1.1 Dissertation Objective

Since their debut in the early part of the twentieth century, synthetic polymers have pervaded every aspect of our daily lives. Polymers are unique in that the properties can be tuned over an enormous range by altering the monomer chemistry, polymer molecular weight, and molecular architecture, to name a few parameters. In addition to the seemingly mundane, yet ubiquitous applications such as garbage bags, tires, adhesives, and credit cards, polymers have also been used in highly specialized engineering applications: for example, bullet-proof vests, artificial joints, and gas separation membranes. These latter applications are excellent examples of one of the principal advantages of polymers; namely, the ability to combine two disparate properties, such as mechanical strength and light weight. As the applications become increasingly demanding, polymer scientists and engineers face the challenge of designing and synthesizing new materials, requiring a fundamental understanding of the structure-property relationships that govern the material behavior.

Polymers garner their extraordinary combination of properties from their unique molecular structure; that is, many repeat units (or “mers”) covalently bound into long chains. The chain-like nature of polymers has important implications for the way in which polymers crystallize. Unlike small molecules, metals, minerals, etc. polymers are rarely completely
crystalline. Instead a kinetically arrested morphology consisting of alternating crystalline and amorphous layers a few tens of nanometers thick is typically observed.\textsuperscript{1} Thus, crystallization is a powerful driver of nanoscale structure in polymers.

Block copolymers are another important tool for creating nanostructures in polymers. In a block copolymer two or more runs (or blocks) of chemically distinct mer units are connected by covalent bonds. The balance between repulsive forces between the chemically dissimilar units and the entropic penalty associated with chain stretching can produce an array of nanoscale structures.\textsuperscript{2,3} The phase behavior of block copolymers is described by the interblock segregation strength ($\chi N$) and the block volume fractions ($\phi$). Combining crystallizable blocks into the block copolymer architecture greatly increases the complexity of the system due to the competition between crystallization and block incompatibility. When the segregation strength is low, crystallization and melting dominate the phase behavior. On the other extreme, where $\chi N$ is large, microphase separation precedes crystallization on cooling and the crystallites are forced to form within the preexisting microdomains.

Styrenic triblock copolymer thermoplastic elastomers (TPEs), which combine a degree of melt processability and solid-state elasticity, are perhaps the first and most successful commercial application of block copolymers.\textsuperscript{4} With the correct block lengths, block incompatibility gives rise to discrete (polystyrene) hard domains embedded in a rubbery matrix. The major drawback of styrenic TPEs is that, although the polystyrene domains are labile at elevated temperatures, the materials remain microphase separated, making processing difficult and energy intensive. Bishop and Register demonstrated that block copolymers with composite crystalline-glassy hard domains, wherein the phase behavior was controlled by crystallization and the glassy blocks, provided a route to easily processable homogeneous melts and robust
This dissertation expands on this concept using block copolymers comprising more commercially relevant chemistry (i.e., anionic polymerization of butadiene, styrene, and isoprene). The goal is to elucidate fundamental structure-property relationships which govern the performance of TPEs with crystalline-glassy composite domains. Furthermore, this work explores the use of a 6-arm star architecture for improving the mechanical performance of TPEs with crystalline, glassy, and composite crystalline-glassy hard domains.

On the other extreme, strongly segregated crystalline-rubbery diblock copolymers are investigated. The study focuses on the interplay between the microdomain structure determined by block incompatibility and the crystal texture and thickness. The crystalline blocks are hydrogenated atactic polynorbornene, which complements the existing reports on crystalline-amorphous diblocks, which rely heavily on polyethylene and poly(ethylene oxide). Finally, the structure and properties of hydrogenated tactic polynorbornenes are investigated and contrasted with those of hydrogenated atactic polynorbornene.

1.2 Dissertation Organization

The relevant background information on polymerization mechanisms, block copolymers, semicrystalline polymers, and TPEs is presented in Chapter 2. Experimental techniques, including polymer synthesis, and molecular, morphological, and mechanical characterization are detailed in Chapter 3. Chapter 4 covers the design of block copolymer TPEs using the known segmental interaction parameters and theoretical phase diagram. Synthetic procedures for preparing linear and star block copolymer TPEs with crystalline, glassy, and rubbery blocks by anionic polymerization, chlorosilane coupling, and catalytic hydrogenation are discussed in
detail. Particular attention is paid to the chlorosilane coupling and hydrogenation reactions with the goal of preparing precisely defined macromolecular architectures with minimal uncoupled material. The processability and mechanical performance of the linear block copolymer TPEs with crystalline-glassy composite hard domains and homogeneous melts is compared to that of triblock copolymers having either crystalline or glassy hard domains in Chapter 5. The merits of the composite hard domains and the importance of the identity of the crystalline block are discussed. Chapter 6 builds on these findings by examining the behavior of 6-arm star block copolymers. The mechanical performance of the 6-arm stars is compared against the analogous linear polymers from Chapter 5.

Chapter 7 covers a series of crystalline-rubbery diblock copolymers with microphase separated melts. The implications of confined crystallization are discussed in the context of the crystallite orientation and thickening. Hydrogenated tactic polynorbornene (hPN) homopolymers are investigated in Chapter 8. This system provides an unusual opportunity to study the influence of tacticity on the structure and thermal properties because the isotactic, syndiotactic, and atactic forms of hPN are all semicrystalline. Finally, the findings of Chapters 4–8 are summarized in Chapter 9. Recommendations for future work are also outlined.
1.3 References


Chapter 2

Background

This chapter presents the fundamental concepts which form the bedrock of this thesis. The concept of “living” polymerization, the term for a set of synthetic techniques which enable the preparation of block copolymers, will first be introduced. Two polymerization mechanisms, anionic polymerization and ring-opening metathesis polymerization, will be discussed. A general discussion of block copolymers and the phenomenon of microphase separation will follow. The chapter will introduce the behavior of crystalline homopolymers and crystalline blocks in block copolymers. Finally, the largest commercial application of block copolymers, thermoplastic elastomers, will be reviewed.

2.1 Living Polymerization

Polymers are long chain-like molecules made up of many repeating units or mers. There are two general strategies for assembling long, linear chains from small molecule monomers: (1) addition (chain-growth) polymerization wherein chains grow from one end to the other by adding one monomer at a time, or (2) condensation (step-growth) polymerization wherein difunctional monomers initially react to form short chains (dimer, trimer, tetramer, etc.) which retain two functional groups per molecule; long chains are formed by condensation of these shorter chains (e.g., trimer + tetramer = heptamer). Though industrially relevant, the statistical
nature of the latter approach does not lend itself to well-defined architectures, such as the block copolymers and star polymers studied herein, and will not be discussed further. Certain “living” types of addition polymerization are better suited to the controlled synthesis requirements of this work.

Livingness refers to the activity of the growing chain end; the most fundamental requirement for a polymerization to be considered living is that it should be free of intrinsic reaction pathways which terminate or transfer the active site on the living end of the chain. An additional requirement for the synthesis of well-defined polymers with predictable, narrow molecular weight distributions is rapid and complete initiation—that is, the reaction of the initiating species with the first monomer should be faster than the addition of subsequent monomers. A polymerization reaction which satisfies these two criteria will produce a collection of chains, equal in number to the number of initiator molecules, with approximately the same number of mers in each chain (i.e., a narrow molecular weight distribution). The persistence of the living end after the monomer has been consumed permits the synthesis of block copolymers by charging a second (third, fourth, etc.), chemically dissimilar monomer. A number of polymerization chemistries can be made to fit the preceding description; this dissertation will employ two of them: anionic polymerization and ring-opening metathesis polymerization.
2.1.1 Anionic Polymerization

First reported around the turn of the 20th century, the unique aspects of anionic polymerization were initially recognized by Ziegler in the 1930s. Two decades later, anionic polymerization was the first mechanism to be described as living. Now, a century after its discovery, the control over the molecular weight and distribution of hydrocarbon polymers afforded by anionic polymerization remains unsurpassed. The living end consists of a carbanion and a complementary cation, typically an alkali metal. A variety of initiators based on lithium, sodium, or potassium have been routinely employed, but the secondary and tertiary isomers of butyllithium (s-BuLi and t-BuLi, respectively) are now the most common due to their commercial availability as solutions of specified concentration in hydrocarbon solvents. These organometallic compounds, and the living polymers prepared therefrom, are extremely reactive (t-BuLi is pyrophoric); thus, molecular oxygen and protic impurities (such as water) must be rigorously excluded from the polymerization environment. Initiators must be handled under high vacuum or inert atmosphere, and polymerizations must be conducted in purified aprotic solvents such as aliphatic and aromatic hydrocarbons, ethers, and tertiary amines. The polarity of the reaction medium is a key parameter in determining the kinetics and products of the polymerization reaction, as will be discussed below. Suitable monomers include styrene and its derivatives, dienes, (meth)acrylates, and heterocyclic compounds. This work employs the common commercial monomers styrene, 1,3-butadiene, and isoprene; these three monomers and their corresponding repeat units are shown in Figure 2.1.
Figure 2.1. Anionic polymerization monomers and repeat units.

The mechanism for anionic polymerization of butadiene initiated by $t$-BuLi is illustrated in Figure 2.2. Polymerization begins with nucleophilic attack on a conjugated double bond by the initiator, labeled 1. One carbon-carbon double bond is consumed during initiation and each propagation step. Two modes of addition are possible during propagation of butadiene: 2a represents 1,4-addition, in which the remaining double bond is located in the backbone and can be either cis or trans, while 2b shows 1,2-addition, which produces a pendant vinyl group. The situation is similar for isoprene which can also undergo 3,4-addition; styrene has only one mode of addition (see Figure 2.1) since the phenyl ring is not susceptible to attack by the carbanion. Note that the mode of addition of the final unit, which bears the anion, is undetermined until the next monomer is added. Anionic polymerization of dienes produces a random copolymer of the various mer units, the ratio of which is determined by the reaction conditions. In apolar hydrocarbon solvents the lithium counter ions are tightly bound and strong interactions between the living ends lead to clustering and aggregation; the 1,4 mode of addition is favored under
these conditions. Polar species (e.g., ethers or tertiary amines) can be used to better solvate the living ends increasing their ionic character, leading to an increase in the vinyl (1,2 and 3,4) modes of addition.\textsuperscript{2}

Figure 2.2. Mechanisms of initiation (1) and propagation (2a and 2b) of anionic polymerization illustrated for the polymerization of butadiene initiated with $t$-BuLi and terminated with a generic proton source labeled “R-H”.

All three of the monomers described here polymerize essentially to complete conversion. Provided that impurities have been rigorously excluded, the living carbanions can be preserved long after the monomer has been exhausted. Block copolymers can be synthesized by sequential addition of chemically distinct monomers; the living polymer functions as a “macroinitiator” to initiate and polymerize subsequent monomer charges. Anionic polymerization can be terminated in a controlled manner by adding a proton source (such as an alcohol) or an electrophile.

The advent of anionic polymerization, among other chemistries, has enabled the synthesis of precisely-defined non-linear macromolecular architectures. Star polymers are one of the best-
studied examples. In general, a star polymer comprises three or more linear polymer “arms” covalently bonded at one end to a central core. Among the available techniques for synthesizing star polymers, living anionic polymerization remains popular due to exquisite control over the architecture and molecular weight distribution of both the arms and the star.\(^4\)-\(^7\) Many important aspects of the physics of branched homopolymers were first investigated using model star polymers prepared by anionic polymerization.\(^8\)-\(^13\) In addition to model branched polymers, the exquisite control afforded by anionic polymerization also enables the synthesis of complex branched architectures such as block copolymer stars, where each arm comprises runs of two or more chemically dissimilar repeat units.\(^4\)-\(^7\)

Two general methodologies are available for synthesizing star polymers using anionic polymerization, “core-first” and “arm-first”. In the core-first strategy the arms are polymerized directly from a multifunctional initiator. To date, multifunctional anionic initiators have struggled to meet the stringent requirements for synthesizing well-defined star polymers.\(^14\) Moreover, this method does not permit independent characterization of the arms. The arm-first approach has been more fruitful. As the name implies, the arms are synthesized first and linked via reaction of the terminal active site with a multifunctional coupling agent.\(^4\)-\(^7\) Thus, narrow-distribution arms can be prepared using established techniques employing commercially available initiators (e.g., isomers of butyllithium) and characterized directly. Coupling is achieved using either difunctional monomers or multifunctional terminating agents. In the former case, the addition of a small amount of a difunctional monomer, such as divinylbenzene, produces a crosslinked microgel core from which the arms radiate. However, the number of arms is inherently broadly distributed and difficult to control.
The best control over the arm number (referred to herein as the star functionality, $n$) and distribution is achieved by terminating the polymerization with a coupling agent of specified functionality, $x$. Using this strategy the number of arms in each star is, ideally, precisely determined by the number of functional groups on the coupling agent ($n = x$). Two classes of multifunctional terminating agents are commonly employed in conjunction with anionic polymerization. Halomethyl benzene derivatives have been used, though the coupling efficiency of halomethyl benzenes, particularly chloromethyl benzenes, can be limited by side reactions such as lithium-halogen exchange.\textsuperscript{4,5,15} Side reactions can yield stars of both higher ($n > x$) and lower ($n < x$) functionality than intended, making isolation of a single species difficult. Bromomethyl benzenes are less prone to side reactions, but are reserved primarily for coupling polymers synthesized in polar solvents at sub-ambient temperatures, such as poly(alkylmethacrylate)s and poly(2-vinylpyridine).\textsuperscript{4,5,15-17} In addition, the highest functionality bromomethyl benzene reported to date has $x = 6$ and suffers from poor solubility in solvents compatible with anionic polymerization.\textsuperscript{16,17} On the other hand, coupling with chlorosilanes proceeds without side reactions,\textsuperscript{4-7} making them the preferred coupling chemistry for living anionic polymers. Well-defined star polymers with narrow arm number distributions have been produced using chlorosilane coupling agents with up to $x = 128$.\textsuperscript{18}
2.1.2 Ring-Opening Metathesis Polymerization

Ring-opening metathesis polymerization is an addition polymerization process by which cyclic olefins are enchained into a polymer. In the mid-1950s researchers discovered that cyclic olefins, such as norbornene and cyclopentene, could be polymerized by activated transition metal complexes.\textsuperscript{19,20} Early Ziegler-Natta type catalysts were ill-defined and polymerizations were non-living. It was recognized early on that, unlike anionic polymerization, all of the double bonds in the monomer were conserved in the polymer backbone. The driving force for the polymerization is the opening of the ring and the release of ring strain rather than the conversion of double bonds into single bonds. As with any reaction, the Gibbs free energy change, given by
\[
\Delta G = \Delta H - T \Delta S,
\]
where \( T \) is temperature and \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy of polymerization, respectively, must be negative for the polymerization to proceed. The release of ring strain drives the reaction forward (i.e., towards polymer), and is balanced by the entropic cost of enchaining many monomers into each macromolecule. Thus, the degree of ring strain is crucial, and only highly strained cyclic olefins can be polymerized to complete conversion. The bicyclic monomer norbornene and its substituted derivatives fit this description, and are the monomers of choice for this work.

A decade and a half after the initial observations, following the discovery of the metathesis reaction between two small molecule olefins, Hérisson and Chauvin first put forth the mechanism for the metathesis process.\textsuperscript{21} The mechanism for ring-opening metathesis polymerization is illustrated in Figure 2.3 with norbornene as the monomer. The process begins with a metal carbene and its associated ligands “L”. The metal center, denoted “M”, becomes active when a ligand dissociates; the electron-rich carbon-carbon double bond on the monomer can then associate with the open site on the metal (1). The metal carbene and the associated
cyclic monomer unit then form a metalallocyclobutane intermediate (2), which rearranges, opening the ring (3) and inserting the monomer between the metal complex and the organic fragment and regenerating the metal carbene (4). Steps 1-4 are repeated many times to produce a polymer with the metal carbene constituting the active end of the chain. Non-living initiators suffer from spontaneous loss of metal activity (termination) and (intra- or intermolecular) chain transfer. Chain transfer can occur when the double bonds in the backbone of the polymer coordinate to the metal center and undergo acyclic metathesis, which scrambles the molecular weight distribution.

**Figure 2.3.** Ring-opening metathesis polymerization mechanism illustrated with a generic metal center “M” with generic ligands “L” and norbornene as the monomer. X=Y represents the terminating agent.
Initiators capable of living ring-opening metathesis polymerization (ROMP) have been developed by Schrock and Grubbs, who, with Chauvin, won the 2005 Nobel Prize in Chemistry for their work. Schrock’s initiators were based on tungsten, and later molybdenum; the latter has been found to be more tolerant of functional groups and is generally preferred. These initiators make use of two alkoxide ligands and an imido ligand to withdraw electron density from the metal center and tune activity. Chain transfer is suppressed by the steric bulk of the ligands. The Mo-based initiator 2,6-diisopropylphenylimidoneophyldene molybdenum(VI) bis(t-butoxide), used in this work, gives excellent control over the molecular weight and distribution, but is highly sensitive to oxygen, moisture, and other polar moieties. Grubbs and coworkers have developed a series of Ru-based initiators which are more tolerant of polar functionalities making them more stable and expanding the palette of available monomers. The so-called “first-generation” Grubbs initiator, used in this work, is based on Ru and makes use of bulky tricyclohexylphosphine ligands which can reversibly dissociate from the metal center to yield the active site.

Trialkyl phosphines can be added to polymerizations initiated by W, Mo, or Ru to modulate the rate of polymerization; these ligands reversibly bind to the active site on the metal center as shown in the initial step of Figure 2.3. This measure is necessary to produce narrow molecular weight distributions with the first-generation Grubbs initiator, which suffers from sluggish initiation. ROMP with either of these classes of initiators has been shown to be living, and the preparation of block copolymers by sequential monomer addition is straightforward. ROMP initiated by either Mo or Ru-based initiators can be controllably terminated through the addition of a double-bond-containing terminating agent, denoted X=Y in Figure 2.3. The role of the terminating agent is to deactivate the metal and remove it from the
chain end. Schrock-type initiators are terminated with aldehydes through a “Wittig-like” mechanism, where X is an organic fragment and Y is atomic oxygen. Ru-initiated ROMP is typically terminated with ethyl vinyl ether, which places a methylene group at the chain terminus.²²

2.2 Block Copolymers

The advent of living polymerization techniques, and in particular anionic polymerization, has given rise to the field of block copolymers. A block copolymer is a polymer chain containing long uninterrupted runs, or blocks, of two or more chemically distinct mer units connected by covalent bonds. Of the innumerable possible block copolymer architectures the simplest is a linear A-B diblock copolymer comprising two linear blocks, A and B, connected end-to-end. Despite their apparent simplicity, A-B diblocks can be an extremely powerful platform for the trained materials scientist or engineer. Consider two polymers with disparate, but desirable properties; for example, A might be permeable to a particular species of interest, while B is mechanically strong. If A and B homopolymers are simply blended together they are likely to phase separate, leading to a macroscopically heterogeneous material with A-rich and B-rich regions.²⁶ Such a system is poorly controlled and clearly far from an ideal engineering material. If the A and B monomers are polymerized simultaneously, yielding a statistical copolymer (A-\textit{stat}-B), the properties of the resulting material will be intermediate between homopolymer A and homopolymer B.²⁷ In the context of this example, A-\textit{stat}-B would show both low permeability and poor strength. However, if instead A and B are incorporated into a block copolymer (e.g., by sequential polymerization of A followed by B or vice versa) the properties of both blocks can be retained.²⁷-²⁹
The key distinction in the preceding example is the phenomenon of microphase separation in the block copolymer. As in the homopolymer blend case, there is an enthalpic penalty associated with contacts between the chemically distinct A and B blocks, which can be minimized by separating the system into A-rich and B-rich domains. However, the covalent connection between the blocks imposes both an entropic penalty as the blocks are forced to stretch orthogonal to the interface and a length scale for separation, which is on the order of the radius of gyration of the polymer \( R_g \approx 10–100 \text{ nm} \).\(^{30}\) The resulting equilibrium state reflects a balance between the enthalpic and entropic contributions and depends on the block copolymer composition (in terms of volume fraction, \( \phi \)), and the segregation strength \( \chi N \), where \( \chi \) is the Flory-Huggins interaction parameter and \( N \) is the total degree of polymerization. Both \( \phi \) and \( N \) can be tuned through the polymerization stoichiometry, while \( \chi \) is set by the choice of mer units.

In principle, \( \chi \) captures the purely enthalpic contribution of contacts between dissimilar segments and should be inversely proportional to \( T \). In practice, the functional form is found\(^{26,31}\) to be \( \chi = \alpha / T + \beta \), where \( \alpha / T \) represents the enthalpic contribution and \( \beta \) is entropic in nature.\(^{32}\) For model hydrocarbon polymers, the segmental interactions are purely repulsive, so \( \chi > 0 \) and decreases with increasing \( T \).

It follows that when the segregation strength \((\chi N)\) in the melt (i.e., above any glass transition and melting temperatures, \( T_g \) and \( T_m \), respectively) is low and the blocks will be intimately mixed (disordered). As \( \chi N \) is increased (by changing temperature, increasing the molecular weight, or choosing less compatible monomers) the system will eventually microphase separate. It should be noted that for a given diblock \( N \) and \( \phi \) are fixed (modulo thermal expansion) and only a modest range of \( \chi N \) can be accessed by changing \( T \); a series of diblocks is required to access a broad range of \( \chi N \) and \( \phi \). The boundary between the disordered and ordered
states is called the order-disorder transition (ODT). The location of the ODT and the resulting microphase-separated morphology depends on $\phi$. For a symmetric diblock\textsuperscript{33} ($\phi_A = \phi_B = 0.5$), the ODT occurs at $(\chi N)_{\text{crit}} = 10.5$, while for an A/B blend\textsuperscript{26} the critical segregation strength for macrophase separation is $(\chi N)_{\text{crit}} = 2$ (where $N$ for the blend is defined for a single component), illustrating the importance of the covalent block junction. Just above $(\chi N)_{\text{ODT}}$, an appreciable fraction of the B segments remain dissolved in the A-rich domains and vice versa; the purity of the domains is lowest near the interface and highest in the center, as depicted in Figure 2.4. Further increasing $\chi N$ increases the domain purity, sharpening the interfaces.

![Figure 2.4](image_url)

\textbf{Figure 2.4.} Illustrations of the morphology and A-segment concentration profiles as a function of the segregation strength $\chi N$.\textsuperscript{26}
In the microphase-separated state self-consistent field theory (SCFT) calculations\textsuperscript{33,34} and experiments\textsuperscript{35} have been used to thoroughly map out the phase behavior of A-B diblock copolymers. Figure 2.5 depicts the theoretical phase diagram for A-B diblock melts.\textsuperscript{26} Near the symmetric point A-B the morphology is a 1-dimensional periodic array of lamellae (L). As the composition becomes increasingly asymmetric, the interfaces curve towards the minority phase, giving rise to network phases (gyroid, G, and orthorhombic, O\textsuperscript{70}), hexagonally packed cylinders (C), and spheres on a body-centered cubic lattice (S). The phase diagram for an A-B diblock is symmetric about $\phi = 0.5$, provided the diblock is conformationally symmetric—i.e., the statistical segment lengths ($b$) of the two blocks are equal. The characteristic periodicity ($d$) of these structures is predicted\textsuperscript{31} to scale as $d \sim bN^{2/3} \chi^{1/6}$, and the characteristic size of the A and B domains can be calculated from $d$, $\phi$, and the geometry of the microdomains.
Figure 2.5. Self-consistent field theory phase diagram and primary morphologies for conformationally symmetric, monodisperse A-B diblock copolymers. S represents body-centered cubic spheres, C is hexagonally packed cylinders, G is the bicontinuous gyroid, and L is lamellar.

In real systems there is almost always some degree of conformational asymmetry between the blocks. The effects of conformational asymmetry have been investigated by SCFT calculations; over the range of experimentally accessible degrees of asymmetry ($b_A/b_B = 1–2$) the position of the ODT envelope ($\chi N_{\text{ODT}}$) and the identity and sequence of the ordered phases
shown in Figure 2.5 are unaffected. However, the boundaries between ordered phases are skewed toward higher volume fractions of the stiffer block (larger $b$). A larger statistical segment length means that the trajectory of the chain is correlated over longer distances, which translates to more elongated chain conformations. In a block copolymer the entropic penalty for stretching is smaller for the block with larger $b$, as is the interfacial area per chain. Thus, morphologies which place the less flexible block on the concave side of the interface display wider regions of stability, while the converse is true of morphologies in which the interfaces curve toward the more flexible block.

The breadth and shape of the molecular weight distribution (quantified through the dispersity, $D = M_w/M_n$, where $M_w$ and $M_n$ are the weight and number average molecular weight, respectively) can also have profound effects on the phase behavior.\textsuperscript{37-39} Theoretical calculations show that as $D$ increases, $(\chi N)_{ODT}$ decreases, indicating that dispersity stabilizes the ordered phases.\textsuperscript{37} The broad distribution in segregation strength also leads to substantially more segmental mixing in the ordered states of the polydisperse melts at a given average $\chi N$.\textsuperscript{38} Thus, it is clear that if access to the disordered state or formation of highly pure microdomains are priorities, as is the case in this work, then the dispersity should be minimized. Living polymerization techniques such as anionic polymerization or ROMP are capable of achieving dispersities approaching the resolution limit of gel permeation chromatography ($D \rightarrow 1.01$), the standard method used to measure molecular weight and distributions.

Given the richness of the phase behavior in simple A-B diblock copolymers, it is easy to see that the possible microdomain morphologies quickly become innumerable when the complexity of the polymer increases. For example, a full description of the phase behavior of a triblock copolymer with three chemically distinct blocks (A, B, and C) requires two volume
fractions, three binary $\chi$ parameters, the total $N$, and the block sequence (i.e., ABC, BCA, or BAC). Non-linear macromolecular architectures add yet another layer of complexity.\textsuperscript{41,42} Figure 2.6 illustrates just a few of the possible block sequences and architectures for block copolymers containing two or three chemically distinct repeat units. Of particular importance for this work are A-B-A triblock copolymers, A-B-C-B-A pentablock terpolymers, and the closely related symmetric star block copolymers (A-B)$_n$ and (A-B-C)$_n$.

\textbf{Figure 2.6.} Example architectures containing two or three chemically distinct mers.\textsuperscript{41}
2.3 Semicrystalline Polymers

Semicrystalline polymers account for a staggering proportion of the global market for synthetic polymers; just two semicrystalline polymers (polyethylene and *isotactic* polypropylene) constitute nearly half of polymer production in the U.S.\(^4^3\) This work makes extensive use of two semicrystalline polymers: polyethylene and hydrogenated polynorbornene. Some of the salient features of the structure and resulting properties of semicrystalline polymers are reviewed in the following section.

2.3.1 Semicrystalline Homopolymers

The long-chain nature of polymers produces a unique semicrystalline structure with characteristic length scales spanning from Å to μm (Figure 2.7).\(^4^4\) At the atomic scale, the organization of the mer units in the crystalline regions look like any other crystalline material; the atoms are arranged on a regular lattice. The fundamental building block of the crystal structure is the unit cell which is described by three edge lengths \((a, b,\) and \(c)\), ranging from a few Å to a few nm, and three angles \((\alpha, \beta,\) and \(\gamma)\) as illustrated in Figure 2.8. The unit cell contains all of the necessary symmetry elements and atomic positions to completely describe the crystal. By convention the polymer backbones, or crystal stems, lie along the \(c\)-axis. It is possible for a single chemical repeat unit to give rise to multiple crystal structures, known as polymorphism.\(^4^5\)
Figure 2.7. Hierarchical structure of semicrystalline polymers from unit cell (a), to lamellae (b), and spherulite (c).\textsuperscript{44}

Figure 2.8. Generalized unit cell (left) and the orthorhombic unit cell of polyethylene\textsuperscript{45} (right).
To be incorporated into a crystallite, a run of consecutive mers must adopt a regular backbone conformation. Crystallization of these short segments is rapid compared to the time required to disentangle and extend the entire chain. As portions of the chain crystallize, topological constraints become trapped, further retarding the dynamics. The interplay between thermodynamics and kinetics results in an alternating morphology of plate-like crystallites separated by regions of amorphous polymer (Figure 2.7b). Instead of adopting the thermodynamically favored fully extended conformation, chains are forced to fold, weaving back and forth between the crystalline and amorphous phases, as depicted in Figure 2.9. A single chain need not reenter the same crystallite each time, and may be incorporated into several different crystals. The alternating crystalline-amorphous structure grows radially from a nucleus in three dimensions to form superstructures called spherulites (Figure 2.7c) which grow until they impinge on each other and fill the entire sample.

**Figure 2.9.** Illustration of the crystal fold surface.⁴⁶
Lamellar crystallites can reach very large lateral dimensions (hundreds of nm to μm), but the thickness in the direction of the polymer backbone (crystal stems, coincident with the c-axis of the unit cell by convention) is typically limited to a few tens of nm. The crystal thickness \( t_c \) is a function of the thermal history and is related to the melting point \( T_m \) through the Gibbs-Thomson equation, written for lamellae of large lateral extent:

\[
T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta H_{m,100} \rho_c t_c} \right)
\]

where \( T_m^0 \) is the equilibrium melting point (in absolute units) of an infinitely thick crystal, \( \Delta H_{m,100} \) is the melting enthalpy of 100% crystalline polymer, and \( \rho_c \) is the density of the crystal. The highly non-equilibrium chain conformations near the interface (shown in Figure 2.9), and the density mismatch between the crystalline and amorphous phases contribute to the interfacial energy penalty \( \sigma \). The fundamental concept underlying equation [2.1] is that the melting point is depressed by the creation of the crystalline-amorphous interfaces; thicker crystals have less interfacial area per unit volume and are thus thermodynamically favored. Though the semicrystalline state is kinetically arrested, the crystals can thicken, particularly when annealed close to \( T_m \), as the system evolves to minimize its free energy.\(^{47,48}\)

2.3.2 Mechanical Properties of Semicrystalline Polymers

The alternating crystalline-amorphous morphology described above confers unique mechanical properties which distinguish semicrystalline polymers from glassy thermoplastics. The mechanical properties of polyethylene, a tough plastic, are relevant for this work. An idealized stress-strain curve for polyethylene in uniaxial extension is shown in Figure 2.10. It bears mentioning that the properties of polyethylene are often modulated by incorporating
counits or long-chain branches, but some general relationships between the crystalline texture and the mechanical properties have been elucidated. The amorphous regions in polyethylene are rubbery at all relevant service temperatures, and the large crystallites form a stiff, percolated stress-bearing network. The Young’s modulus, defined by the initial slope in the elastic region, typically ranges from 50–250 MPa and is sensitive to the degree of crystallinity.49

![Figure 2.10. Idealized stress-strain curve for polyethylene.49](image)

As strain increases, the stress passes through a local maximum (called the yield stress), which corresponds to the onset of plastic or unrecoverable deformation. This is the macroscopic manifestation of a series of nanoscopic deformation mechanisms which occur in the crystalline phase (Figure 2.11).50-53 First, [001] screw dislocations of individual stems are activated and propagate through the crystal to become (hk0)[001] slip dislocations. This process aligns the stems in the direction of the applied load as shown in the center panel of Figure 2.11. Eventually the large plate-like crystallites begin to break up54-57 (right hand side of Figure 2.11) and the
fragments slip past each other. Though tie molecules—chains which span the amorphous layer to connect two crystallites—keep the material from failing for another several hundred percent strain, this typically marks the end of the article’s usefulness. Upon releasing the stress, the initial structure (left hand side of Figure 2.11) is not recovered, and deformation beyond the yield point is largely unrecoverable. Structural relaxation is arrested by fusion of the exposed lateral surfaces of adjacent crystal fragments and crystallization of oriented segments (originating in either the crystalline or amorphous phases).

Figure 2.11. Deformation mechanisms in semicrystalline polyethylene.
2.3.3 *Semicrystalline Block Copolymers*

Incorporating a crystalline block into a block copolymer leads to incredibly rich but complex behavior. The phase behavior and morphology is determined by the delicate balance between the two competing thermodynamic driving forces: crystallization and block incompatibility. Relevant to this work are block copolymers with a single crystalline component.

When the melt is disordered (i.e., the segregation strength at the crystallization conditions \((\chi N)_c < (\chi N)_{ODT}\)), the phase behavior is dictated entirely by crystallization and melting. Much of this thesis relies on this concept. The solid-state morphology of these diblocks is found to be lamellar across a wide range of crystalline block volume fractions due to the strong propensity for polymers to form plate-like crystallites.\(^{58-61}\) The morphology resembles that of the semicrystalline homopolymer where the non-crystalline block is confined to the amorphous regions between crystallites as shown in Figure 2.12. Theory\(^ {62}\) and experiments\(^ {58,61}\) both find that the characteristic spacing scales as \(d \sim N N_a^{-1/3}\), where \(N\) is for the total diblock and \(N_a\) is for the amorphous block.
**Figure 2.12.** Possible scenarios for crystallization in crystalline-amorphous diblock copolymers. Melt structures are on the left and solid-state structures are on the right. Upper right panel represents the crystallization-driven morphology observed for disordered or weakly segregated systems. Lower right panel represents crystallization which is templated or confined within the existing microdomain structure.
Several different scenarios arise when the melt is microphase-separated prior to crystallization. If the melt is weakly segregated, \((\chi N)_c \gtrsim (\chi N)_{ODT}\), and the amorphous block is rubbery during crystallization, the melt-state morphology undergoes substantial restructuring upon crystallization to accommodate the strong preference for lamellar crystallites.\(^{59,63-70}\) Termed “breakout”, the resulting morphology resembles the lamellar structure described in the preceding paragraph; however, the domain spacing is found to depend on the crystallization conditions.\(^{59,64,67-69}\) For the crystals to break out of the microdomain structure, crystallizable segments must diffuse through the amorphous domains to add to the growing crystal. The associated energy penalty can be overcome in the weak segregation limit, particularly if crystallization is slow.

The melt morphology can be “templated” in diblocks with rubbery amorphous blocks by increasing the segregation strength. At intermediate \(\chi N\), interblock mixing is suppressed (Figure 2.4), and measures of the structure, such as small-angle x-ray scattering and transmission electron microscopy, indicate that the solid-state structure closely resembles that of the melt, save for the occasional crystallite spanning multiple domains.\(^{70,71}\) The long-range order is somewhat diminished due to distortions caused by crystallization. Crystallization can be rigorously confined within the microphase-separated structure using very strong segregation: \((\chi N)_c \gg (\chi N)_{ODT}\).\(^{68-72}\) Confined and templated systems are structurally similar, and the distinction lies primarily in the crystallization kinetics. Truly confined crystallization in isolated microdomains (spheres and cylinders) proceeds by homogeneous nucleation, that is, each microdomain must be nucleated separately, whereas templated crystallization exhibits sigmoidal crystallization kinetics indicative of a spreading-growth crystallization habit more typical of heterogeneous nucleation.\(^{68-71}\) This distinction is not definitive for classifying the behavior of
lamellar-forming diblock copolymers because a single nucleus can crystallize many microdomains by traversing grain boundaries and dislocations.\textsuperscript{73,74}

Crystallization can also be mechanically confined (hard confinement) by using an amorphous block which is glassy at the crystallization conditions ($T_g > T_c$, where $T_c$ is the crystallization temperature). The microdomain morphology in the melt state is set when the amorphous block vitrifies and the crystals are strictly confined to the crystallizable domains, be they spherical, cylindrical, gyroid, or lamellar.\textsuperscript{71-72,75-82} Interestingly, though the glassy phase leads to strictly confined crystallization, the structure is not entirely unperturbed. Loo and Register\textsuperscript{78} showed that the density change associated with crystallization in a series of polymers was accommodated by affine contraction of the entire system, despite the high modulus of the glassy microdomain matrix ($\approx 3$ GPa). Moreover, in a polymer with cylindrical semicrystalline domains they found that the crystal orientation in neighboring microdomains was correlated due to microdomain deformation associated with crystallization.\textsuperscript{83}

The various modes of crystallization in crystalline-amorphous block copolymers have important implications for the crystal orientation. The morphology of diblocks crystallized from disordered or weakly segregated melts resembles that of semicrystalline homopolymers, namely the crystal stems lie perpendicular to the crystalline-amorphous interface (top right of Figure 2.12). This situation arises from the need to match the interfacial area per chain on either side of the interface. In templated or confined systems the crystal orientation is such that the fast-growth direction ($b$-direction in polyethylene) is aligned with the longest dimension of the microdomain to permit maximal crystal growth.\textsuperscript{78-79,81} In lamellar microdomains the $c$-axis is often parallel to the microdomain interface as depicted in the bottom right panel of Figure 2.12.\textsuperscript{72,78,81,84} This texture is preferred because the resulting crystal thickness need not be
commensurate with the thickness of the domain; however, the two remain coupled through the constraint that the block junctions be localized to the domain interfaces.\textsuperscript{81} This situation leads to an equilibrium crystal thickness, which is expected to depend on the thickness of the crystalline domain. In poly(ethylene oxide) (EO) the orientation of the crystal stems with respect to the interfaces can range from parallel to perpendicular depending on the crystallization conditions.\textsuperscript{75-77}

2.4 Thermoplastic Elastomers

A thermoplastic elastomer (TPE) is a material which combines the incongruent properties of solid-state elasticity and melt processability. Elasticity, characterized by highly reversible deformation to large strains (Figure 2.13), is uniquely polymeric, arising from the coil-like conformations of long polymer chains.\textsuperscript{85} Traditional elastomers are prepared by chemically cross-linking (vulcanizing) a collection of entangled, rubbery chains to create a network of covalent bonds which spans the entire system. Once set, such a material cannot be recycled or reprocessed into a new article and must be discarded or repurposed. TPEs incorporate a degree of melt processability by employing a network of physical cross-links which anchor the rubbery chains at the service temperature, but are labile at elevated temperatures.\textsuperscript{86}
Figure 2.13. Example stress strain curve for an elastomer.\textsuperscript{85}

Though the earliest TPEs were not the well-defined block copolymers reviewed above, A-B-A triblock copolymers are now synonymous with TPEs. Triblocks synthesized by anionic polymerization were perhaps the first—and remain the most successful—commercial application of block copolymers.\textsuperscript{87,88} Indeed, the development of the field of block copolymers owes much of its early success to the investigation of block copolymer TPEs. Poly(styrene-\textit{b}-isoprene-\textit{b}-styrene) and poly(styrene-\textit{b}-butadiene-\textit{b}-styrene), shortened to S-I-S and S-B-S, triblock copolymers were first investigated by Shell Chemical as additives to improve the green strength of synthetic \textit{cis}-1,4-polyisoprene and high 1,4-polybutadiene rubbers prior to vulcanization.\textsuperscript{87} Researchers quickly recognized the exceptional properties of the neat triblock copolymers, and moved to commercialize the first block copolymer TPEs.
The theory of microphase separation was developed soon after to explain the remarkable elastomeric behavior in the unvulcanized state. It is now well-established that the system microphase separates into morphologies with discrete S domains embedded in a continuous polydiene matrix (Figure 2.14). Theory\textsuperscript{89} has shown that A-B-A triblock copolymers adopt the same microphase-separated morphologies as their diblock analogs, and both spherical and cylindrical S domains are commonly found in commercial TPEs, though the latter is more common. Below their glass transition temperature ($T_g$) the S domains are rigid, and since the triblock architecture ensures that both ends of each rubbery block are anchored to an S domain, the material is elastomeric. It is important that the S domains are discrete because large, interconnected domains lead to plastic, rather than elastic, solid-state behavior.

**Figure 2.14.** Illustrations of styrenic TPEs in the solid and melt states.
Above the $T_g$ of the S blocks both domains are fluid and the material can flow. However, the strong segregation required to create sufficiently pure S domains renders the ODT inaccessible. If the segregation strength is too weak, the S domains will be plasticized by the polydiene, degrading the solid-state mechanical properties. For example, the ultimate strengths of S-I-S triblocks (with nominally 20% S) with thermotropic ODTs estimated\(^9\) at 190 and 140 °C were only 60% and 8% of the limiting value found for higher molecular weights.\(^9\) This tradeoff makes simultaneously attaining homogeneous melts and good use-temperature mechanical properties in styrenic TPEs infeasible. Thus, amorphous A-B-A triblock copolymer TPEs remain microphase-separated during melt processing. In order for the material to flow over macroscopic length scales, S blocks must be extracted from the S domains in which they reside at equilibrium and transported through the diene matrix (Figure 2.14); this process is energetically costly. Consequently, styrenic triblock copolymer TPEs have high melt viscosities and elasticities.\(^28\)

Truly emulating the processability of thermoplastics requires access to single-phase melts. Using crystallization, rather than block incompatibility, to drive physical crosslinking can provide pure hard domains (crystals) irrespective of the segregation strength. Thus, compatible block chemistries can be chosen to permit access to easily processable homogeneous melts above the melting point of the semicrystalline blocks ($T_m$). In the solid state, the rubbery component is anchored to the crystallites; the astute reader will already have noted the similarity between the concept of physical cross-linking and the morphology of semicrystalline homopolymers described above. Crystallinity can also add a degree of solvent resistance which is not attainable in completely amorphous materials like styrenic TPEs.\(^92-94\)
Building off the extensive work on styrenic TPEs, early semicrystalline TPEs employed anionic polymerization followed by catalytic hydrogenation to prepare C-B-C triblock copolymers with semicrystalline polyethylene (linear low-density polyethylene derived from hydrogenated low-vinyl polybutadiene, E) C blocks. Hydrogenated isoprene or mid-vinyl butadiene (poly(ethylene-alt-propylene), EP, or poly(ethylene-ran-butylene), EB, respectively) were used as the rubbery mid block. Homogeneous melts and qualitatively elastomeric properties were indeed achieved; however, the crystalline blocks led to higher moduli and permanent sets than their fully amorphous counterparts. A triblock with higher-crystallinity linear polyethylene blocks, studied by Myers and Register, showed elastomeric properties at small strains but significant yielding above 350% strain. These adverse effects are a consequence of two factors: (1) crystallization tends to produce interconnected crystals of large lateral extent (Figure 2.7), which have a greater effect on the modulus than discrete domains, and (2) the crystals are prone to yielding via chain pullout and fragmentation as described above (Figure 2.11).

More complex block architectures have been devised to improve the performance of crystalline-rubbery TPEs. Hotta et al. synthesized block copolymers using crystalline isotactic polypropylene (iPP) blocks and regioirregular polypropylene (rPP) rubbery blocks which displayed elastomeric behavior. They found that the tensile strength of an iPP-rPP-iPP-rPP-iPP pentablock copolymer was four times that of the analogous iPP-rPP-iPP triblock. The improvement was attributed to the central iPP block inhibiting chain pullout from the crystals, though interestingly, the pentablock architecture did not reduce the permanent set.

The natural extension of this approach is segmented or multiblock copolymers with alternating crystalline and amorphous blocks of the general form (-C-B-)ₙ. Commercial
examples include thermoplastic poly(ether esters) and polyolefin block copolymers (OBCs). Poly(ether esters)\(^{102}\) are made by condensation of short (ca. 1000 g/mol) hard and soft segments, and in the case of poly(ether esters), homogeneous melts are attainable with relative ease.\(^{103}\) The high hard block contents necessary to produce sufficiently high melting points give rise to high tensile strength; however, the accompanying high modulus, low yield strain, and appreciable permanent set at modest strains limit their utility. OBCs comprise alternating blocks of ethylene/\(\alpha\)-olefin copolymers with low (crystalline blocks) and high (rubbery amorphous blocks) \(\alpha\)-olefin content.\(^{104-108}\) Weak block incompatibility allows access to homogeneous melts, but imposes little restriction on the polyethylene crystallization. As a result, good ultimate properties can be attained, but the Young’s moduli are relatively high and strongly temperature-dependent. In a similar vein, Koo et al. found that well-defined \((-E-\text{EP}-)_n\) multiblock copolymers show elastomeric strain-hardening behavior only when crystallized from a microphase-separated melt or when \(n \geq 10.\(^{109}\)

Given that crystallization-driven phase behavior can afford drastically improved processability while glassy domains provide superior mechanical performance, efforts have been made to incorporate both crystalline and glassy components into a single material. The simplest approach is to use an A-B-C triblock copolymer where A is glassy and C is crystalline.\(^{96,110,111}\) However, strong microphase separation is still necessary to produce pure glassy domains, and the large-strain mechanical properties are limited by the response of crystals. Bates and coworkers studied two symmetric block copolymer architectures of the general form X-B-X where X represents either alternating glassy-crystalline-glassy-crystalline-glassy\(^{112}\) or glassy-crystalline-glassy\(^{113,114}\) block sequences and B was rubbery EP. In all cases the total hard block (X) content was relatively high (\(\approx 50\%\)), leading to high Young’s moduli and permanent sets, but
homogeneous melts were obtained and the observed strain-hardening behavior was attributed to the effective reinforcement of the crystals by the adjacent glassy domains.

A simpler C-A-B-A-C pentablock architecture was studied by Bishop and Register$^92$ using ring-opening metathesis polymerization of various norbornene derivatives, where C is crystalline, A is glassy and B is rubbery. Incorporating the glassy blocks had a strong beneficial impact on the mechanical properties; a triblock with crystalline end blocks displayed plastic behavior, while the pentablocks were soft elastomers with single-phase melts (Figure 2.15). This qualitative transformation was attributed to the role of glassy block aggregation during crystallization which limits the lateral dimensions and connectivity of the crystallites and provides mechanical reinforcement.
Figure 2.15. Uniaxial stress-strain curves for TPEs with different physical cross-linking domains: a triblock with crystalline end blocks (hPN-triblock), a triblock with glassy end blocks (hPMTD-triblock-H), and two pentblocks with the crystalline-glassy-rubbery-glassy-crystalline block sequence (Pentablock-10 and -14). The total hard block (crystalline + glassy) block content was held constant at 20 wt%.  

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2.5 References


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Chapter 3

Experimental Methods

This chapter provides relevant information pertaining to the synthesis and characterization of the polymers studied in this work. Synthetic procedures are provided for anionic and ring-opening metathesis polymerizations as well as catalytic hydrogenation. Molecular characterization by gel permeation chromatography, nuclear magnetic resonance spectroscopy, and Fourier transform infrared spectroscopy are described. A description of differential scanning calorimetry, small-angle and wide-angle x-ray scattering, and atomic force microscopy for thermal and morphological characterization follows. Methods for assessing the solid-state mechanical performance by uniaxial tensile testing and dynamic mechanical thermal analysis are presented. Finally, rheological measurements of the flow behavior of block copolymer melts will be introduced. Detailed descriptions of the specialized procedures are reserved for subsequent chapters.
3.1 Polymer Synthesis

Two polymerization chemistries were employed in this work: anionic polymerization and ring-opening metathesis polymerization (ROMP). In all cases the residual carbon-carbon double bonds were removed by catalytic hydrogenation. A general outline of these procedures is given below.

3.1.1 Anionic Polymerization

Before delving into the experimental setup and procedure used for anionic polymerization the hazards must first be stated. Of paramount concern is the potential for fire. The solvents and monomers used for anionic polymerization are both highly volatile and flammable. In addition, the organometallic initiators and cleaning agents employed are highly reactive—chief among them is $t$-BuLi, which is pyrophoric. Finally, the handling of air-free reagents necessitates the use of high-vacuum techniques, cryogenic conditions, and sealed glass vessels and the possibility of overpressurization and ultimately explosion presents a serious hazard.

As stated above, the organometallic reagents used to initiate anionic polymerization (isomers of butyllithium $t$-BuLi and $s$-BuLi, throughout this work) are extremely sensitive to contaminants including oxygen and moisture. Thus, they, along with solvents, monomers, and other reagents, must be handled in an air-free environment. Monomers and solvents, as well as the polymerization reactions, are manipulated on a dual manifold Schlenk line; half of the line was evacuated to $\leq 60$ mtorr using an Edwards mechanical pump, while the other half was continuously fed with $N_2$ gas. Any operations which could not be performed on the line were
conducted in an N\textsubscript{2}-filled MBraun UNIlab glove box operating at <0.1 ppm O\textsubscript{2} and <0.1 ppm H\textsubscript{2}O.

Cyclohexane, benzene, and triethylamine were stirred over diphenylhexyllithium (adduct of BuLi and 1,1-diphenylethylene) and degassed by repeatedly freezing, evacuating, and thawing the flask (freeze-pump-thaw cycles). Tetrahydrofuran was dried over sodium benzophenone ketyl, degassed, and vacuum transferred prior to use. Isoprene and styrene monomers (Sigma-Aldrich) were stirred over \textit{n}-BuLi and \textit{di}-\textit{n}-butylmagnesium, respectively, and degassed immediately prior to use. Butadiene (Airgas) was collected in a graduated trap cooled with liquid nitrogen, warmed up to 0 °C using an ice-water bath, stirred over \textit{n}-BuLi, and used promptly. Coupling agents were used as received and stock solutions were prepared in the glove box.

Each polymerization began by adding the appropriate initiator to a pear-shaped, thick-walled glass reactor (shown in Figure 3.1). Prior to bringing the reactor into the glove box it was equipped with a Teflon stir bar and flame-dried under vacuum. Butadiene polymerizations were initiated with \textit{t}-BuLi (1.7 M in pentane, Sigma-Aldrich), and \textit{s}-BuLi was used to initiate styrene (1.4 M in cyclohexane, Sigma-Aldrich). The reactor was then sealed and moved to the Schlenk line and evacuated. The appropriate solvent was vacuum transferred into the reactor, followed by the first monomer. The reactor was kept frozen on liquid nitrogen and evacuated following each transfer step to remove any air which may have leaked into the line during the transfer.
Polymerizations were conducted at 60 °C under vacuum. After the initial monomer charge was consumed (2 h for polydienes or 1 h for polystyrene), block copolymers were prepared by freezing the reactor contents and vacuum transferring additional monomers (and solvents, if necessary). Following the polymerization of each block, a sample was withdrawn through a side port in the reactor using the apparatus pictured in Figure 3.1b. The final polymer concentration was restricted to 10 wt% throughout. Polymers were isolated by precipitation into methanol.
3.1.2 Ring-Opening Metathesis Polymerization

The initiators used for ring-opening metathesis polymerization are also sensitive to oxygen and moisture (though they do not pose a hazard like BuLi) and must be handled in the glove box. Figure 3.2 depicts the two commercially available ROMP initiators used in this work: the Mo-based Schrock-type\(^1\) initiator 2,6-diisopropylphenylimidoneophyridene molybdenum(VI) bis(t-butoxide) is available from Strem Chemicals and the “1\(^{st}\) Generation” Grubbs\(^2,3\) initiator benzylidene-bis(tricyclohexylphosphine)dichlororuthenium was purchased from Sigma-Aldrich. These will be henceforth referred to simply as the Schrock and Grubbs initiators, respectively. Norbornene (systematic name bicyclo[2.2.1]hept-2-ene, Sigma-Aldrich) and its hydrocarbon derivatives were dried over sodium, degassed by freeze-pump-thaw cycles, vacuum transferred and stored in the glove box. Hydroxyhexafluoroisopropynorbornene (systematic name, 2-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1,1,1,3,3,3-hexafluoropropan-2-ol, abbreviated HFAN, Promerus, LLC) was degassed and stored over 3 Å molecular sieves in the glove box. The reaction solvent, toluene, was purified using an MBraun SPS-Compact solvent purification system.
Polymerizations were conducted in round-bottom flasks in the glove box at ambient temperature. The appropriate initiator was dissolved in toluene and charged to the reactor with the required volume of toluene. The rate of polymerization was modulated by adding 5 equivalents of trialkylphosphine (trimethylphosphine for the Schrock initiator or tricyclohexylphosphine for the Grubbs initiator). The monomers were then charged to the reactor and polymerized. Norbornene (which is a solid at room temperature) was dissolved in toluene prior to adding, while all other monomers were added neat. A final polymer concentration of 4 wt% was targeted. Polymerizations initiated with the Schrock initiator were terminated with degassed propionaldehyde (Sigma-Aldrich) or benzaldehyde (Sigma-Aldrich, used as received). Polymerizations initiated with the Grubbs initiator were terminated with ethyl vinyl ether. Polymers were recovered by precipitation.
\subsection*{3.1.3. Catalytic Hydrogenation}

Anionic polymerization and ROMP both produce unsaturated polymers. Backbone unsaturation, which persists in 1,4-polydienes and ROMP polymers, are prone to degradation by chain scission or cross-linking, and must be removed. Many important physical properties are also altered by hydrogenation; some of these are vital to this work and will be highlighted where appropriate. Hydrogenations were conducted in a 2 L Parr reactor equipped with mechanical stirring, under 400 psi \(\text{H}_2\), unless otherwise noted. Each polymer was dissolved in cyclohexane at a concentration of 2–5 g/L and charged to the reactor with the catalyst. The reactor was sealed, purged with nitrogen, charged with 400–500 psi of hydrogen, and heated to the desired temperature while stirring vigorously.

Most of the polymers reported here were hydrogenated using a supported palladium catalyst (5 wt\% Pd on CaCO\(_3\)). The bimetallic catalyst 3 wt\% Pt–2 wt\% Re supported on a wide-pore SiO\(_2\) (Pt–Re/SiO\(_2\))\(^{4-7}\) was investigated, but used sparingly. Pd/CaCO\(_3\) was used in a 2:1 mass ratio to polymer (including support), while a 0.2:1 ratio was used for Pt–Re/SiO\(_2\). The supported catalysts were removed by filtration. An unsupported Ni–Al catalyst was prepared by first dissolving 1.04 g of as-received nickel(II) 2-ethylhexanoate (78\%, Sigma-Aldrich) in approximately 30 mL cyclohexane in a sealed flask.\(^8,9\) This mixture was sparged with \(\text{N}_2\) before adding 10 mL of triethylaluminum solution (1.0 M in hexanes, Sigma-Aldrich), yielding Al:Ni = 4.25. The active catalyst was immediately charged to the reactor, minimizing exposure to air. The reactor was then charged with \(\text{H}_2\) and heated to 80 °C. This process was repeated until saturation was complete. The polymer solution was stirred over 8 wt\% aqueous citric acid and washed with deionized water to extract the catalyst. Hydrogenation with the homogeneous catalyst carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (Ru(CO)ClH(PPh\(_3\))\(_3\), 99\%,
Strem) was conducted by separately dissolving the polymer and catalyst (200 ppm to polymer) in toluene, charging them to the reactor along with 600 psi H₂, and heating to 160 °C. Ru(CO)ClH(PPh₃)₃ was removed from the polymer by precipitation into methanol.

The reaction progress was monitored by Fourier transform infrared spectroscopy or proton (¹H) nuclear magnetic resonance spectroscopy. The polymer solution was removed from the reactor, concentrated by removing solvent, and precipitated to isolate the product. Polymers were dried in a vacuum oven at a temperature where all of the components were rubbery to remove residual solvent.

3.2 Molecular Characterization

This section introduces the use of gel permeation chromatography, nuclear magnetic resonance spectroscopy, and Fourier transform infrared spectroscopy for characterizing the molecular structure of polymers.

3.2.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC), also known as size-exclusion chromatography, is perhaps the single most powerful tool for characterizing the molecular weight, distribution, and architecture of polymers. The heart of the GPC is the columns, which consist of a packed bed of nanoporous beads. Polymers dissolved in a good solvent are passed through the column(s) and are separated based on their hydrodynamic size. As chains flow past the beads, osmotic pressure drives them into the pores. Smaller chains are able to sample more of the pore volume, while larger chains are excluded; thus, the chains elute from largest to smallest. A train of detectors is placed after the columns to characterize the material as it elutes.
The GPC system used for this work comprises two 30 cm Polymer Laboratories PLgel Mixed-C columns (operating at 35 °C). Samples are prepared by dissolving a polymer at approximately 2.5 mg/mL in tetrahydrofuran (THF), then injected into the system via a Rheodyne 7725i manual injector. The mobile phase (THF) is maintained at a flow rate of 1 mL/min by a Waters 515 HPLC pump. This work makes use of three detectors: a UV absorbance detector (Waters 2489, λ = 254 nm, room temperature), a three-angle light scattering (LS) detector (Wyatt Technologies miniDAWN TREOS, λ = 658 nm, room temperature), and a differential refractive index (RI) detector (Wyatt Optilab T-rEX, λ = 658 nm, 25 °C). Specific refractive index increments (dn/dc) were measured on narrow-distribution homopolymers using a Wyatt Optilab rEX (λ = 658 nm, 25 °C). UV absorption coefficients (ε) at 254 nm were also measured using the GPC and Beer’s law; the sample concentration was calculated using the RI signal and the known dn/dc.

The RI signal is directly proportional to the mass concentration of polymer in solution and can thus be used to directly visualize the shape of the molecular weight distribution and compute the dispersity (Đ). The number-average and weight-average molecular weights (M_n and M_w, respectively) can also be calculated from the RI signal alone, though some ancillary measurements are needed. The system is calibrated by a series of well-characterized, narrow-distribution, linear polymer standards (anionically synthesized polystyrene is used here) to generate a calibration curve of molecular weight versus elution time, as shown in Figure 3.3. The following functional form was used to fit the calibration data in the present work:

\[
\log(M_{cal}) = A + Bt_v + C(t_v - t_p)^n
\]

[3.1]

where \(t_v\) is the elution time and \(A, B, C, t_p,\) and \(n\) are fit constants. The non-linear term \(C(t_v - t_p)^n\) only applies for \(t_v > t_p\). The functional form is empirical and depends on the GPC system.
Since the separation is based on size, not molecular weight, applying equation [3.1] to a different polymer gives the calibrant-equivalent molecular weight \( M_{cal} \) rather than the absolute \( M \). The universal calibration\(^\text{15}\) concept can be used to compute absolute molecular weights for many different polymers from a single calibration curve. The volume of a polymer coil in solution is proportional to the product \( M[\eta] \), where \([\eta]\) is the intrinsic viscosity. Thus, for a given \( t_v \), the quantity \( M[\eta] \) should be constant regardless of the identity of the polymer. The Mark-Houwink-Sakurada (MHS) equation, in turn, gives the intrinsic viscosity in terms of the molecular weight: \([\eta] = KM^a\). The exponent, \( a \), is essentially constant for linear random coil...
polymers in a good solvent. Equating $M[\eta]$ for the analyte and calibrant, applying the MHS expression, and solving for the absolute molecular weight of the analyte, $M_{an}$, gives:\textsuperscript{14}

$$M_{an} = M_{cal} \left( \frac{K_{cal}}{K_{an}} \right)^{1/(1+a)} = \frac{M_{cal}}{r_{an}}$$

Equation [3.2] indicates that the elution time-molecular weight curves for the calibrant and the analyte are parallel. Figure 3.3 illustrates this point with linear polystyrene, polyisoprene, and polybutadiene. The proportionality constant, can be measured by preparing a single polymer of the chemistry of interest and calculating $M_{cal}$ using equation [3.1] and measuring $M_{an}$ using an absolute method (e.g., light scattering): $r_{an} = M_{cal}/M_{an}$. Equation [3.2] can then be used to find $M_{an}$ for any polymer of the same chemistry. The $r$ factors determined for linear polymers are not valid for star polymers which are more compact in solution, and thus follow a different MHS expression from their linear analogs.\textsuperscript{16,17} The absolute molecular weights of block copolymers can be calculated using the $r$ factors for the constituent blocks and a combining rule; the Chang combining rule is used here:\textsuperscript{14,18,19}

$$r_{BCP} = \sum w_i r_i$$

where $w_i$ is the weight fraction of component $i$.

The absolute weight-average molecular weight can also be measured using online light scattering. Equation [3.4] relates the scattered intensity as a function of the scattering angle ($2\theta$) to the absolute molecular weight and concentration ($c$) of the polymer in solution:

$$\frac{K^* c \left( \frac{dn}{dc} \right)^2}{R_0} = \frac{1}{M_wP(\theta)} + 2A_c c$$

where the LS detector directly measures the Rayleigh ratio ($R_0$), which proportional to the scattered intensity, and $K^*$ is a collection of constants.\textsuperscript{20} The contribution of the second virial
coefficient ($A_2$) term is modest for the molecular weights of interest; therefore, a constant value of $A_2 = 5 \times 10^{-4}$ mol mL/g² was used throughout this work.²¹ The specific refractive index increment ($dn/dc$) describes how the refractive index of the solution changes with $c$, and thus depends principally on the polymer-solvent pair. At low concentrations $dn/dc$ is a constant. If $dn/dc$ is known, it can also be used to calculate the instantaneous $c$ from the differential refractive index signal ($\Delta n$) measured by the RI detector: $c = \Delta n/(dn/dc)$. Thus, the determination of absolute $M_w$ by light scattering requires only one input, $dn/dc$. Moreover, LS analysis is valid regardless of the macromolecular architecture.

The form factor, $P(\theta)$, describes the angular dependence of the scattering for an individual polymer molecule in solution. For Gaussian chains the form factor is given by the Debye equation:

$$P(\theta) = \frac{2}{q^2 R_g^2} \left( e^{-q^2 R_g^2} - 1 + q^2 R_g^2 \right)$$

$$q = \frac{4\pi n}{\lambda} \sin(\theta)$$

where $R_g$ is the radius of gyration and $q$ is the magnitude of the momentum transfer vector, and $n$ is the refractive index of the medium.²⁰ The analysis software ASTRA 6 (Wyatt Technologies) was used to calculate $M_w$. The software computes $M_w$ at each time point during the elution using equations 3.4 and 3.5 and averages over the entire distribution. In some instances, particularly when $M_w \leq 10$ kg/mol where $R_\theta$ is independent of $\theta$, the calculation fails; in these cases the more robust Zimm equation²² (equation [3.7]) was used.

$$\frac{K^* c}{R_\theta} \left( \frac{dn}{dc} \right)^2 = \frac{1}{M_w} \left( 1 + \frac{q^2 R_g^2}{3} \right) + 2A_2 c$$
Block copolymers can also be analyzed by light scattering. The true weight-average molecular weight for block copolymers were calculated in ASTRA using weight-fraction weighted $dn/dc$ values:\textsuperscript{23}

$$
(dn/dc)_{BCP} = \sum w_i (dn/dc)_i \tag{3.8}
$$

### 3.2.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used to determine the composition of the polymers studied herein. Polymers were dissolved in the appropriate deuterated solvent (chloroform-d, 1,4-dioxane-d$_8$, tetrahydrofuran-d$_8$, or 1,1,2,2-tetrachloroethane-d$_2$) at approximately 5 mg/mL for $^1$H NMR or >20 mg/mL for $^{13}$C NMR. $^1$H NMR spectra were collected on a Bruker AVANCE spectrometer operating at 500 MHz; $^{13}$C NMR spectra were collected at 125 MHz. More details will be provided as necessary in subsequent chapters.

### 3.2.3 Fourier Transform Infrared Spectroscopy

Semicrystalline polymers cannot be analyzed by room-temperature NMR spectroscopy; therefore, the progress of most of the hydrogenation reactions were tracked by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were acquired in transmission using a Nicolet iS50 spectrometer. Polymer films were prepared by drop casting onto polished NaCl disks (Sigma-Aldrich) from dilute solutions. Background spectra were subtracted from each sample spectrum to remove the contributions of atmospheric moisture and CO$_2$.

FTIR involves passing a beam of broad spectrum infrared light through a sample and measuring the absorbance as a function of wavelength. IR light is absorbed when its energy (wavelength) matches the resonant energy of a bond vibration in the material. Resonant bond
vibrations that change the dipole moment of the molecule will show up as a peak in absorbance in the FTIR spectrum. This makes FTIR adept at detecting the presence of particular moieties, such as carbon-carbon double bonds. The absorbance \( (A_i) \) of a particular vibration is given by Beer’s Law: \( A_i = \varepsilon_i c_i l \), where \( \varepsilon_i \) and \( c_i \) are the molar extinction coefficient and the concentration of the species \( i \), and \( l \) is the sample thickness.\(^{24}\) Quantitative analysis by FTIR is challenging because the molar extinction coefficient depends on the particular vibration in question.

The relevant peaks for unsaturated polybutadiene are: \textit{cis}-1,4-addition at 735 cm\(^{-1}\), 1,2 at 911 cm\(^{-1}\), and \textit{trans}-1,4 at 966 cm\(^{-1}.\)\(^{25-27}\) For polyisoprene the peaks relevant for unsaturation are \textit{trans}-1,4 at 815 cm\(^{-1}\), \textit{cis}-1,4 at 843 cm\(^{-1}\), 3,4 at 887 cm\(^{-1}\), and 1,2 at 909 cm\(^{-1}.\)\(^{25,26}\) Aromatic vibrations for polystyrene are located in two broad bands at 1600–2000 cm\(^{-1}\) and 3000–3200 cm\(^{-1}\), as well as strong individual peaks at 700, 906, 943, 964, and 979 cm\(^{-1}.\)\(^{28}\) The polymers of interest have very low contents of 1,2-polybutadiene (\(\approx8\%)\), 3,4-polyisoprene (\(\approx7\%)\), and 1,2-polyisoprene (<1%). Saturating the 1,4-polybutadiene is the most critical as residual unsaturation will limit the crystallinity of the eventual polyethylene block; therefore, the peak at 966 cm\(^{-1}\) was used to determine the degree of saturation. Complete saturation of polystyrene blocks, which comprises a maximum of 20 wt\% of the material, is not critical though it will affect the glass transition temperature and segmental interaction parameter of the glassy block. Figure 3.4 shows example spectra for a block copolymer containing polybutadiene, polyisoprene, and polystyrene blocks before and after hydrogenation. The vibrations associated with the \textit{cis} and \textit{trans} double bonds in polynorbornene and its derivatives appear at approximately 740 and 966 cm\(^{-1}\), respectively.\(^{29}\) The \textit{trans} carbon-carbon double bonds in polynorbornene hydrogenate more slowly than do the \textit{cis} C=C bonds,\(^{29,30}\) so the 966 cm\(^{-1}\) peak was again used to track the reaction progress.
Figure 3.4. FTIR survey spectrum of a block copolymer containing polybutadiene, polyisoprene, and polystyrene (a) and an expanded view of the fingerprint regions of the unsaturated and saturated derivatives normalized to the absorbance at 1377 cm\(^{-1}\).
Quantitative analysis can be performed by using an internal reference peak, which is present throughout the course of the reaction. The methylene peak near 1377 cm⁻¹ was used as the internal reference, since all of the polymers studied have at least one methylene per repeat unit in both the unsaturated and saturated forms. The fractional degree of saturation \( f_{\text{sat}} \) for a peak located at \( \nu \) cm⁻¹ is given by:

\[
f_{\text{sat}} = 1 - \delta \left( \frac{A_{\nu}}{A_{1377}} \right)_{\text{sat}} \left( \frac{A_{1377}}{A_{\nu}} \right)_{\text{unsat}}
\]

where the factor \( \delta \) accounts for the change in the number of methylene units upon hydrogenation, assuming that all methylene groups have identical extinction coefficients at 1377 cm⁻¹. In practice equation [3.9] works well for intermediate levels of hydrogenation, but overlapping peaks and difficulties in determining the baseline complicate the analysis as the reaction nears completion. Thus, the hydrogenation reaction of both anionic and ROMP polymers is considered complete when the olefinic peaks are no longer discernible from the baseline (Figure 3.4), corresponding to \( \geq 99\% \) saturation.

### 3.3 Thermal and Morphological Characterization

This section presents the techniques used to probe the atomic and nanoscale characteristics of block copolymers. Differential scanning calorimetry is discussed for the characterization of crystallization and melting and glass transitions. The theory of x-ray scattering is covered, followed by the concepts of wide- and small-angle scattering and equipment pertinent to this work. Finally atomic force microscopy is introduced.
3.3.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a powerful technique for studying thermal transitions such as crystallization and melting and glass transitions. DSC measures the heat flow into or out of a sample as the temperature is raised or lowered. Measurements were made with a PerkinElmer DSC7 equipped with a Type II intracooler. A scan rate of 10 °C/min was used unless otherwise noted. The temperature was calibrated using the onset of melting of mercury ($T_m = -38.83$ °C) and indium ($T_m = 156.60$ °C). The enthalpy was calibrated with indium ($\Delta H_m = 28.45$ J/g). Polymer samples (5–10 mg) were encapsulated in crimped aluminum pans.

The DSC7 functions on the principle of power compensation. There are two nominally identical furnaces, each with its own temperature sensor and resistive heater, embedded in a thermostated block (see Figure 3.5). The sample pan is placed in one furnace and an empty aluminum pan is placed in the other. A temperature program is applied to both furnaces simultaneously (heat is applied by platinum wire heaters and the block supplies cooling) and the instrument measures the difference in power required to achieve the same temperature in both furnaces. Since the sample and reference furnaces are never perfectly matched, an identical temperature program is run with an empty pan in both furnaces and subtracted from the sample data. The raw heat flow signal can be converted to heat capacity ($C_p$) by dividing by the ramp rate and the sample mass.
Figure 3.5. Schematic of the dual furnace configuration of the DSC7. The sample and reference sides are marked “S” and “R”, respectively, “2” denotes the temperature sensor, and “1” denotes the heating element.32

Figure 3.6 shows a DSC trace of a diblock copolymer containing an amorphous block (hydrogenated poly(HFAN), hPHFAN) and a semicrystalline block (hydrogenated polynorbornene, hPN). The most prominent feature is the sharp melting peak ($T_m = 137.8$ °C). The melting enthalpy ($\Delta H_m$) is calculated by integrating the melting endotherm using a baseline formed by extrapolating the melt data to lower temperature until it intersects the solid-state heat capacity (dotted line in Figure 3.6). The degree of crystallinity ($w_{c,DSC}$) of the crystalline component is given by:

$$w_{c,DSC} = \frac{\Delta H_m}{w_x \Delta H_{m,100}}$$  \hspace{1cm} [3.10]

where $w_x$ is weight fraction of the crystalline component and $\Delta H_{m,100}$ is the melting enthalpy of 100% crystalline polymer. The two semicrystalline polymers relevant to this work are
polyethylene$^{33}$ ($\Delta H_{m,100} = 277 \text{ J/g}$) and hPN$^{30}$ ($\Delta H_{m,100} = 86 \text{ J/g}$). Glass transitions are identified by step changes in $C_p$. The inset in Figure 3.6 shows an expanded view of the glass transition. The glass transition temperature ($T_g$) taken as the midpoint in the step change in $C_p$ measured on heating, 42.5 °C in the figure.

Figure 3.6. Differential scanning calorimetry trace of hPN-hPHFAN-46 (see Chapter 7 for details) on heating. Inset shows an expanded view of the glass transition.
3.3.2 X-Ray Scattering

A firm understanding of x-ray scattering is vital to this work. This section introduces important fundamental concepts and provides descriptions of the x-ray equipment used.

3.3.2.1 General Theory

X-rays possess several key properties which make them ideal for studying the structure of matter on length scales well below the wavelength of visible light. First, the wavelength of x-rays is commensurate with interatomic distances ($\lambda \approx 1 \, \text{Å}$). This distinguishes x-ray scattering from the concepts of light scattering outlined above; in light scattering experiments the wavelength of the incident radiation ($\lambda = 658 \, \text{nm}$ for the Wyatt instrument) is larger than the scattering object (polymer coil, $R_g \approx 10–100 \, \text{nm}$). Second, x-rays, like visible light, are scattered by electrons and the coherent component of the scattering—which carries structural information—typically dominates. Third, x-rays with a narrow wavelength distribution can be generated, manipulated, and detected using lab-scale equipment.

When x-rays interact with matter, they cause electrons to vibrate in unison with the electric component of the field. Scattering is the process by which a vibrating electron (charged particle) in turn emits an isotropic wave of x-ray radiation.\textsuperscript{34,35} If the wavelength and phase of the incident and emitted radiation are equal, the scattering process is called coherent. Coherent scattering makes up the bulk of x-ray scattering events, and is treated in the following discussion. Incoherent scattering is when the phases of the incoming and outgoing radiation are uncorrelated, and is responsible for diffuse background scattering.

Many coherent scattering events occur within a collection of atoms, the scattered waves will interfere with each other. Components of scattered waves which are in phase will interfere
constructively (i.e., the measured intensity is high), while components which are out of phase cancel out. The constructive interference pattern for a well-ordered structure with characteristic size \(d\), is described by Bragg’s Law:

\[ n\lambda = 2d \sin \theta \]  

where \(n\) is the integer order of reflection and \(2\theta\) is the scattering angle. A geometric illustration of Bragg’s Law is shown in Figure 3.7. Two waves are reflected off of parallel planes “1” and “2”, if the extra distance travelled by the lower wave \((2b = 2d \sin \theta)\) is equal to an integer multiple of the wavelength \((n\lambda)\) then the waves interfere constructively, creating a peak in the intensity. Thus, the characteristic dimensions of the structure \((d)\) can be calculated by measuring the scattered intensity as a function of \(\theta\).

\[ \text{Figure 3.7. Illustration of x-ray diffraction and Bragg’s Law.}^{34} \]
The scattering angles at which peaks appear depend on $\lambda$ of the incident radiation. The wavelength dependence is often removed, particularly in the case of small-angle x-ray scattering, by using the magnitude of the momentum transfer vector, $q$, defined in equation [3.6], with $n = 1$ for x-rays. Combining equations [3.6] and [3.11] gives the simple relationship for the characteristic dimension:

$$d = 2\pi / q$$

[3.12]

Equation [3.12] shows the reciprocal relationship between the scattering measurement and the characteristic dimensions in the material; in fact, x-ray scattering measures the Fourier transform of the real-space structure.\(^{35}\)

3.3.2.2 Wide-Angle X-Ray Scattering

It is clear from equation [3.11] that when x-rays are used, scattering angles ranging from a few degrees to tens of degrees will contain information about interatomic distances.\(^{34}\) This is referred to as wide-angle x-ray scattering (WAXS). WAXS is used extensively in polymer science to study the atomic scale structure of semicrystalline polymers. The highly regular structure characteristic of crystalline materials gives rise to a series of sharp diffraction peaks which fall in the range of $2\theta \approx 3$–60°, as shown for hPN\(^{30}\) in Figure 3.8. Each peak corresponds to a plane of atoms within the crystal structure. Planes are described using dimensionless reciprocal coordinates called Miller indices ($hkl$). The interplanar spacing ($d_{hkl}$) is geometrically related to the Miller indices, and the real-space unit cell dimensions $a$, $b$, and $c$. Equation [3.13]\(^{36}\) shows the relationship for an orthorhombic lattice, such as that of polyethylene.\(^{37}\)

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

[3.13]
Figure 3.8. One-dimensional WAXS pattern of hPN with diffraction peaks denoted by arrows and the amorphous scattering demarcated by dotted lines.\textsuperscript{30}

The amorphous regions of semicrystalline polymers also contribute to the WAXS pattern. Though there is no long-range order in the amorphous regions, there is a range of preferred interatomic spacings. Scattering from these short-range correlations gives rise to a broadly distributed region of scattering often referred to as the amorphous halo. The amorphous scattering for hPN is outlined by dotted lines in Figure 3.8 (2θ ≈ 15–25°). The degree of crystallinity ($w_{c,WAXS}$) can be calculated from the relative areas of the crystalline and amorphous contributions to the WAXS pattern as shown in equation [3.14].\textsuperscript{38,39}
In general, the intensity of the amorphous scattering ($I_{amorphous}$) is easier to fit empirically and is thus commonly used to calculate $w_{c,WAXS}$. Quantitative differences between $w_{c,DSC}$ (equation [3.10]) and $w_{c,WAXS}$ arise from difference in the way the two techniques account for the contributions of the crystalline-amorphous interface.\textsuperscript{39-41}

### 3.3.2.3 Small-Angle X-ray Scattering

Due to the reciprocal relationship between $q$ and $d$, measurements at smaller angles give information about progressively larger real-space structures. Small-angle x-ray scattering (SAXS) can be used to gather structural information on length scales of 1–100 nm, which corresponds to the dimensions inherent to the crystalline-amorphous spacing in semicrystalline polymers and block copolymer microdomains. In SAXS, constructive interference arises from collections of many atoms (domains), rather than individual atoms. Scattering arises from electron density differences between different domains in a material. Both the size and shape of these domains, and their relative arrangement in space contribute to the scattering pattern. The size and shape of the domains is described by the form factor $P(q)$, much like how a polymer coil is described in light scattering. However, bulk polymer samples contain dense collections of these domains (crystallites or microdomains) unlike the isolated polymer coils in dilute solution encountered in light scattering. The relative arrangement of domains is described by the structure factor $S(q)$. The scattered intensity is often represented as:\textsuperscript{42}

$$I(q) \propto P(q)S(q)$$  \hfill [3.15]

In dense arrays, $S(q)$ gives rise to Bragg peaks which dominate $I(q)$.
At equilibrium, microphase-separated block copolymers exhibit highly ordered structures, as introduced in Chapter 2. The structure factors for common block copolymer morphologies have been calculated and are typically presented as ratios of the peak positions to the position of the primary peak ($q^*$), as shown in Figure 3.9. The characteristic spacing between domains (microdomains or crystallites) is calculated from $q^*$ using equation [3.12]. For body centered cubic spheres peaks are located at $q/q^* = 1, \sqrt{2}, \sqrt{3}, \sqrt{4},$ and $\sqrt{5}$. Hexagonally packed cylinders give rise to peaks at $q/q^* = 1, \sqrt{3}, \sqrt{4}, \sqrt{7},$ and $\sqrt{9}$. Alternating lamellae have peaks at integer multiples of $q^*$ (i.e., $q/q^* = 1, 2, 3, 4,$ and $5$). The higher order peaks are damped by paracrystalline distortions in the structure as well interfacial smearing due to mixing and undulations. This is particularly apparent in SAXS patterns of semicrystalline polymers; the primary peak is typically broad and the higher order peaks are either weak or absent because of the inherently broadly distributed lamellar spacing.
Figure 3.9. SAXS patterns for common block copolymer morphologies. Structure factor peaks indicated by arrows.\(^{43}\)

3.3.2.4 Instrumentation

Four different x-ray systems were used during the course of this work: two WAXS instruments and two SAXS instruments. Key features of each system are presented in this section. X-ray were supplied to all four systems by one of two PANalytical PW3830 x-ray generators equipped with PANalytical C-Tech long fine focus Cu x-ray tubes. Copper has two
relevant characteristic x-rays $K_\beta$ and $K_\alpha$ superimposed on a broad continuum (bremsstrahlung). The CuK$_\alpha$ x-rays ($\lambda = 1.5418$ Å) were preferentially selected using various methods depending on the instrument.

One-dimensional WAXS patterns were collected using a Phillips-Norelco wide-range goniometer, which operates in the $\theta$-$2\theta$ geometry, equipped with a scintillation detector. CuK$_\alpha$ x-rays were selected using an Advanced Metals Research graphite focusing monochromator and pulse-height analysis at the detector. The scattering angle was calibrated via a quartz standard. Polymer films (100–200 μm thick) were prepared using a melt press and supported on a glass slide.

A W. H. Warhus Statton pinhole camera, schematized in Figure 3.10, was used to collect two-dimensional WAXS patterns. Wavelength discrimination and collimation are achieved by a Huber graphite monochromator and two 500 μm pinholes, respectively. Samples were mounted in brass cells and loaded into a custom-built hot stage controlled by an Omega CN76000 controller. The camera was evacuated to <1 torr to minimize absorption and scattering due to air. One of two systems was used to acquire data. Patterns were either collected with Kodak SO-230 storage phosphor screens and read by a Storm 820 scanner (GE Healthcare) or collected with Fuji BAS-IP MS storage phosphor screens and read by a Typhoon FLA 7000 IP scanner (GE Healthcare). The scattering angle was approximately calibrated using unoriented high-density polyethylene (HDPE) or isotactic polypropylene (iPP), or precisely calibrated using NaCl as described elsewhere.$^{44}$ The Statton camera is also capable of collecting SAXS data, but the dimensions of the camera preclude access to the $q$-range relevant for this work.
One-dimensional SAXS patterns were collected on an Anton-Paar compact Kratky camera. The CuK$_\beta$ line was selectively removed by passing through a Ni filter. The Kratky camera delivers a slit-collimated beam, which has the advantage of high incident flux. Samples were mounted in copper cells with either mica (20 μm thick) or aluminum foil (25 μm) windows and loaded into a custom-built hot stage controlled by a Fuji PYX-4 controller. The camera was evacuated to ≤200 mtorr to reduce the contribution of air scattering and absorption. Scattered x-rays were detected with a one-dimensional position-sensitive detector (MBraun OED-50M). Further wavelength discrimination (beyond that of the Ni filter) was provided by pulse-height discrimination at the detector. The raw data was corrected for detector sensitivity and positional linearity, empty beam scattering, sample thickness and transmittance, placed on an absolute scale ($I/I_0$) via a polyethylene standard, and desmeared for slit length.$^{45}$ The scattering angle was calibrated using silver behenate ($q^* = 1.07626$ nm$^{-1}$).$^{46}$

Two-dimensional SAXS patterns were collected using a point-focusing system designed by Molecular Metrology (“MolMet”). The collimation system employs the “DuMond geometry” comprising two bent triangular Si crystals.$^{47,48}$ The beam is defined and monochromated by successive reflections off of orthogonal Si (111) planes. Samples were loaded into stainless steel
cells with 15 μm-thick aluminum foil windows, which were then inserted into a hot stage controlled by an Omega CN76000 controller. The system was evacuated to ≤200 mtorr to minimize air scattering and absorption. The sample-to-detector distance is 1.5 m, and the detector is an argon-filled two-dimensional multiwire grid.49 The raw data were corrected for detector sensitivity, empty beam scattering, and sample thickness and transmittance (measured by a photodiode positioned on the beam stop). The scattering angle was calibrated with silver behenate.

3.3.3 Channel-Die Alignment

The microdomains of microphase-separated block copolymers were oriented by uniaxial planar extensional flow in a lubricated channel die.50,51 Aluminum dies with channel widths of 0.5 cm or 1 cm were used; a schematic of the die is shown in Figure 3.11. The interior, polymer-contacting surfaces of the die were lubricated with silicon oil (60,000 cSt, trimethylsiloxy-terminated, Gelest, Inc.); this measure mitigates viscous drag from the walls, creating near plug flow of the block copolymer. Block copolymers were first melt pressed into sheets (on a PHI hydraulic press) and cut into small strips with the same width as the channel. The lower portion of the die was assembled and strips where then stacked in the center of the die. The mass of polymer was chosen to fill the die completely and yield the desired final specimen thickness (ca. 1–2 mm). The upper portion of the die was inserted and the assembly was placed on the melt press. The apparatus was heated above the highest melting or glass transition temperature in the system, but below the order-disorder transition temperature (if present) and allowed to equilibrate for 15 minutes. Pressure was then gradually applied until the desired specimen thickness was achieved. The die was held in the press for an additional 15 minutes to allow any
residual stresses to relax. The die was then cooled by either shutting off press heaters or removing the assembly from the press and cooling on the bench top. Excess silicon oil was removed by gently washing with soap and water. Specimens for two-dimensional x-ray scattering analysis (Statton and MolMet) were cut with a razor blade; several sections were stacked to ensure that the sample covered the entire beam footprint.

**Figure 3.11.** Schematic of the channel die used to align block copolymer microdomains. CD is the constraint direction, FD is the flow direction, and LD is the load direction.
3.3.4 Atomic Force Microscopy

Atomic force microscopy (AFM) images were acquired using a Dimension 3000 AFM in tapping mode using force modulation tips (NanoWorld, force constant 1.2–5.5 N/m, resonance frequency = 60–90 kHz). Films were prepared by spin-coating at 3000 rpm from 2 wt% solutions in toluene preheated to 95 °C onto Si wafers at room temperature. Spun-cast films were annealed at 140 °C for 15 minutes on a hot plate. The thickness of the (C-EP)$_2$ film was measured by ellipsometry to be 120 nm. Rapid crystallization of the semicrystalline block copolymers led to dewetting and droplet formation, precluding accurate measurements of the film thickness. Images are 2 μm × 2 μm with a pixel resolution of 512 × 512.

3.4 Mechanical and Rheological Characterization

Methods for characterizing deformation in polymers in both the solid and melt states are presented in this section. Solid-state characterization is conducted in uniaxial extension using various strain protocols. Polymer melts were characterized in steady and oscillatory shear using a rheometer.

3.4.1 Tensile Testing

The room-temperature mechanical properties were characterized in uniaxial extension at room temperature using an Instron 5865. Compression-molded sheets were prepared using a PHI hydraulic press. Samples were loaded into the press between Mylar$^\text{®}$ sheets sandwiched between aluminum plates. Each sample was heated on the press for 5–10 min and then pressed for 5–10 min. The sample and aluminum plates were removed from the press and allowed to cool to room temperature on the bench top (30–45 min). The materials with crystalline end
blocks (which exhibit homogeneous melts) were pressed at 140–160 °C and ≤2 MPa. The materials with glassy end blocks were pressed at 170 °C and 3–6 MPa. The resulting sheets were approximately 300 μm thick. Test specimens were stamped from compression-molded sheets using an ASTM D1708 dogbone die. A constant cross-head speed of 2 in/min (corresponding to an initial strain rate of 0.038 s\(^{-1}\)) was used throughout. Data are presented as engineering stress (\(\sigma = \) instantaneous force/initial cross-sectional area) versus engineering strain (\(\varepsilon = \) change in length/initial length).

Two types of test were performed: strain to break and cyclic strain recovery. Strain to break tests were used to measure the full stress-strain behavior. The Young’s modulus (\(E_Y\), also known as the initial modulus) was measured by fitting a line to the small-strain (\(\varepsilon \leq 3\%\)) portion of the stress-strain curve. The ultimate strength (\(\sigma_\text{u}\)) was taken as the maximum engineering stress reached during the test. The breaking strain (\(\varepsilon_\text{b}\)) was the strain at which the specimen failed. The ultimate toughness (\(T_\text{u}\)) corresponds to the energy per unit volume required to break the specimen and was obtained by integrating the stress-strain curve from \(\varepsilon = 0\) to \(\varepsilon_\text{b}\).

The strain recovery was assessed using the following cyclic strain test procedure: a specimen was strained to a prescribed strain (\(\varepsilon_\text{a}\)), the cross-head was immediately returned to its initial position at the same rate, and the specimen was allowed to rest for 5 min before the process was repeated, increasing \(\varepsilon_\text{a}\). Strains of 25, 50, 100, 150, 200, 300, 400, and 500% were applied to each specimen; Figure 3.12a shows an example of the raw data.
Figure 3.12. Example of raw cyclic strain test data from (E-EP)₂ (a), and an illustration of the residual strains measured therefrom (b).
Two metrics were calculated from the cyclic strain data: the recovery \((R)\) and the hysteresis \((H)\). To calculate \(R\), the residual strain (set, \(\varepsilon_s\)) was measured at two time points for each cycle. For a given cycle, the “initial” set \((\varepsilon_i)\) corresponds to the strain at which the stress first dropped to zero while the cross-head was returning to its initial position. The “final” set \((\varepsilon_f)\) was defined as the strain at which the stress first became non-zero on the subsequent advancing cycle. The 5 minute rest should be sufficient to recover nearly all of the recoverable strain;\(^{52}\) thus, \(\varepsilon_f\) is considered to be the permanent set. These two measures of residual strain are illustrated in Figure 3.12b using the 400% and 500% cycles. The residual strain \((\varepsilon_i\) and \(\varepsilon_f)\) was then recast in terms of the percent recovery:

\[
R = (1 - \varepsilon_i / \varepsilon_a) \times 100\% \tag{3.16}
\]

The initial and final recovery are denoted \(R^i\) and \(R^f\), respectively. The fractional hysteresis measures the amount of energy dissipated as heat during deformation and is calculated by the difference in the areas under the loading and unloading curves normalized by the area under the loading curve.
3.4.2 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) can be used to characterize the temperature and frequency dependence of the small-strain mechanical response of viscoelastic materials. In DMTA a sinusoidal strain profile of the form $\varepsilon = \varepsilon_0 \sin(\omega t)$, where $\omega$ is the frequency and $t$ is time, is applied to the sample and the strain response is measured. The strain amplitude ($\varepsilon_0$) is chosen such that the test is conducted within the linear viscoelastic regime. The stress response can be represented as the sum of an in-phase and out-of-phase component:

$$\sigma = E'\varepsilon_0 \sin(\omega t) + E''\varepsilon_0 \cos(\omega t)$$ \hspace{1cm} [3.17]

The modulus is resolved into the in-phase component or storage modulus ($E'$), and out-of-phase component or the loss modulus ($E''$). The balance between viscous and elastic character is often represented by:

$$\tan \delta = \frac{E''}{E'}$$ \hspace{1cm} [3.18]

where $\delta$ is the phase lag between the applied strain the measured stress. Physically, the value of $\tan \delta$ characterizes the extent to which viscous forces dissipate energy within the material; thus, $\tan \delta$ will be small for elastic materials. For an elastic material $E'$ approaches $E_Y$ as $\tan \delta$ approaches zero.

Here, DMTA was used to probe the temperature dependence of the small-strain modulus using an RSA 3 (TA Instruments). Specimens (approximately 0.3 mm x 1 mm) were cut from compression-molded sheets using a razor blade. During testing the test fixture was enclosed in an environmental chamber purged with dry nitrogen. All tests were conducted in the tensile geometry (fiber-film fixture). Specimens were tested in temperature ramp mode beginning at −100 °C and heating at 2 °C/min. An initial strain amplitude of 0.1% and frequency of 1 Hz were used throughout.
3.4.3 Steady-Shear and Oscillatory Rheology

The rheology of block copolymer melts was characterized using an Anton Paar MCR-501 stress-controlled rheometer. Samples were punched from compression-molded sheets, loaded into the rheometer and heated to 180 °C under nitrogen. The tool was then lowered to the desired position and the melt was trimmed to minimize edge effects. All tests were conducted at 180 °C under constant nitrogen flow. Two types of tests were conducted: steady-shear and small-amplitude oscillatory shear (SAOS). In steady-shear, the viscosity is measured as a function of shear rate. A cone-and-plate fixture (25 mm in diameter with a cone angle of 2°) was used when possible; the advantage of the cone-and-plate fixture is that the shear rate is constant across the entire sample. (C-EP)$_2$ was too elastic to load, necessitating the use of a parallel-plate fixture (also 25 mm in diameter); in this case the torque-weighted average viscosity is reported as a function of the shear rate at the rim. SAOS experiments were conducted to resolve the elastic (G') and viscous (G") components of the shear modulus (much like the DMTA measurements described in the preceding section). The 25 mm parallel-plate fixture was used for SAOS experiments. Isochronal ($\omega = 0.01$ and 0.1 rad/s) strain amplitude sweeps were used to determine the linear viscoelastic region; subsequent frequency sweeps were conducted using a strain amplitude of 1% at the rim.
3.5 References


Chapter 4

Design and Synthesis of Linear and Star Block Copolymer Thermoplastic Elastomers

This chapter details the design and synthesis of thermoplastic elastomers with the block sequence motif crystalline-glassy-rubber. The choice of block sequence and lengths is discussed. Preparation of both linear and star-shaped block copolymer TPEs by anionic polymerization and catalytic hydrogenation is outlined, and specific challenges are addressed. The molecular characteristics of the polymers studied in subsequent chapters are described.

4.1 Block Sequence and Chemistry

The objective of this work is to prepare thermoplastic elastomers (TPEs) which display elastomeric solid-state performance approaching that of commercial styrenic triblock copolymers (e.g., Kratons™) but have easily processable homogeneous melts. As introduced in Chapter 2, melting and crystallization of a crystallizable block can provide a direct, reversible transition between a physically cross-linked solid and a homogeneous melt. However, the mechanical properties of the resulting crystalline domains are inferior to the glassy domains in commercial TPEs. These two attributes—access to homogeneous melts and robust elastomeric mechanical response—can be combined by using block architectures which incorporate both crystalline and
glassy blocks. Of the many possible architectures, the block sequence crystalline-glassy-rubbery-glassy-crystalline, demonstrated by Bishop and Register\textsuperscript{1} is both simple and effective.

If the block lengths are chosen carefully, the material can be disordered above the melting point of the semicrystalline end blocks. As the melt is cooled, crystallization begins to establish the network of physical cross-links characteristic of a TPE. As the end blocks crystallize, the adjacent glassy blocks are drawn to the crystal-amorphous interfaces purely due to chain connectivity. Aggregation and subsequent vitrification of the glassy blocks impedes the growth of the crystallites, limiting their size and connectivity. The result is composite crystalline-glassy domains where the glassy regions are situated between the crystalline and rubbery domains.

Bishop and Register prepared block copolymers by living ROMP of substituted norbornene monomers. The advantage of this system is that the structural similarity between substituted ROMP mers leads to low interblock incompatibility, permitting access to disordered melts at high molecular weights. However, not all of the monomers used are commercially available and the ROMP initiators are expensive. Moreover, the rubbery block (hydrogenated poly(5-hexylnorbornene), hPHN) has a relatively high glass transition temperature ($T_g = -22 \, ^\circ\text{C}$) and low plateau modulus ($E_N^0 = 1.1 \, \text{MPa}$).\textsuperscript{2} This work seeks to expand on the work of Bishop and Register using commercially relevant chemistry, namely anionic polymerization of butadiene, styrene, and isoprene. Hydrogenated high 1,4-polybutadiene (linear low-density polyethylene, E) serves as the crystalline block. Whereas the crystalline block in the prior work was highly crystalline hydrogenated polynorbornene (hPN), the crystallinity ($w_c \approx 0.4$) and melting point ($T_m \approx 100–105 \, ^\circ\text{C}$) of the E blocks are limited by the ethyl branches arising from 1,2 units in the precursor polybutadiene blocks.\textsuperscript{3,4} The glassy block is hydrogenated polystyrene.
(polyvinylcyclohexane, C, $T_g = 145\ ^\circ\text{C}$), and the rubbery block is hydrogenated polyisoprene (poly(ethylene-alt-propylene), EP, $T_g = -60\ ^\circ\text{C}$ and $E_N^0 = 3.45\ \text{MPa}$).

The aim is to further elucidate the important parameters governing the performance of TPEs based on the crystalline-glassy-rubbery motif by comparing the two systems. In addition, this work investigates the use of star block copolymers with glassy-rubbery, crystalline-rubbery, or crystalline-glassy-rubbery arms as a means to further improve the mechanical performance.

### 4.2 Block Lengths

The primary objective in designing TPEs with the block motif E-C-EP is to gain access to homogeneous melts above the polyethylene melting point ($T_m$). To achieve this goal, microphase separation must be avoided. A full description of the phase behavior of a triblock copolymer with three chemically distinct blocks (A, B, and C) requires two volume fractions ($\phi$), three binary interaction parameters ($\chi$), the total number of repeat units ($N$, proportional to molecular weight, $M_n$), and the block sequence.\(^8\) Rigorous treatment of the phase behavior of pentablock terpolymers would require system-specific self-consistent field theory calculations,\(^9\)\textsuperscript{-11} which are beyond the scope of this work.

Instead, the extensive available literature on block copolymers of E, C, and EP was used to guide the design and synthesis of the triblock and pentablock copolymers. In the present case, the block chemistries and sequence have been chosen as outlined above, leaving the individual block lengths as the primary independent variables controlling the phase behavior. Within these constraints a rough estimate of the appropriate block lengths was made by mapping each pair of blocks onto the generalized self-consistent mean field theory phase portrait for A-B diblock
copolymers (Figure 4.1).\textsuperscript{12,13} Only two variables ($\phi$ and $\chi N$) are required to describe the phase behavior, and the calculations can be done by hand.

**Figure 4.1.** Theoretical phase diagram\textsuperscript{13} for an A-B diblock copolymer. Symbols connected by lines represent values calculated for the polymers described in Table 4.4 using the pseudo-diblock approach at 20 °C (higher $\chi N$) and 160 °C (lower $\chi N$). Circles denote C-EP pairs, triangles are E-C, and squares are E-EP. Filled symbols indicate $\phi = \phi_C$ and open symbols indicate $\phi = \phi_E$.

First, a relevant composition is chosen. Then the segregation strength at the order-disorder transition ($\chi N)_{ODT}$ is determined from the theoretical phase portrait (Figure 4.1).\textsuperscript{12,13} Experimental data is used to calculate $\chi$ for the components and temperature of interest; it is convenient to work in terms of the interaction energy density $X$ because the arbitrary choice of
reference volume necessary to define $\chi$ is avoided.\textsuperscript{14,15} Equation [4.1] shows the relationship between $X$ and $\chi$, where $\rho$ is the density, $R$ is the gas constant, and $T$ is temperature in absolute units.

$$X = \frac{\chi N \rho RT}{M_n}$$  \hspace{1cm} [4.1]

The limiting $M_n$ which ensures miscibility is then given by:

$$M_{n,max} = \frac{(\chi N)_{ODT} \rho R T_{ODT}}{X}$$  \hspace{1cm} [4.2]

A diblock copolymer with total $M_n \leq M_{n,max}$ will be disordered at $T_{ODT}$.

Using this approach, some simple arguments can be used to guide the choice of block lengths necessary to avoid microphase separation. The binary interaction parameters for the blocks in question are shown in Table 4.1.\textsuperscript{8,16-18} The binary interaction parameters follow the relation: $\chi_{E:C} > \chi_{EP:C} \gg \chi_{E:EP}$. To achieve the desired elastomeric behavior the rubbery block must constitute the majority of the material, while the other two components should be present in roughly equal amounts; in terms of volume fractions $\phi_{EP} > \phi_E \approx \phi_C$. Volume fractions were calculated using the mass densities compiled by Beckingham et al.\textsuperscript{14} It is not obvious \textit{a priori} whether the E-C pair (higher $\chi$) or the C-EP pair (larger $N$) will have a stronger tendency to microphase-separate, so both must be considered to ensure miscibility.
Table 4.1. Binary Interaction Parameter Correlations\textsuperscript{18,a}

<table>
<thead>
<tr>
<th>Binary Pair</th>
<th>$\alpha$ (K)</th>
<th>$\beta \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-C</td>
<td>29.4</td>
<td>-17.4</td>
</tr>
<tr>
<td>C-EP</td>
<td>15.7</td>
<td>-3.6</td>
</tr>
<tr>
<td>E-EP</td>
<td>8.9</td>
<td>-16.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The binary interaction parameter is given by $\chi = \alpha/T + \beta$.

A reference temperature of $T_{ODT} = 160 \, ^\circ C$ is chosen for the following calculations. Treating the more strongly interacting E-C pair and taking the representative case of a symmetric ($\phi_E = \phi_C = 0.5$) diblock, where $(\chi N)_{ODT} = 10.5$, indicates that disordered melts are achieved for $M_n < 13 \, kg/mol$. Using this result and a composite hard block (E and C) content of 20 wt\% (a representative value for TPEs and the same value used by Bishop and Register) limits $M_n$ of an E-C-EP-C-E pentablock copolymer to $\approx 130 \, kg/mol$. Turning to the corresponding C-EP pair and choosing $\phi_C = 0.1$ (where $(\chi N)_{ODT} \approx 45.5$), the limiting $M_{n,max}$ which ensures miscibility for the pentablock is calculated to be 160 kg/mol. These simple calculations show that the phase behavior of the pentablocks is more sensitive to the E-C pair.

The other important consideration is the glass transition temperature ($T_g$) of the glassy domains; in order to achieve the requisite mechanical strength, $T_g$ must be well above the use temperature. The C-domain $T_g$ will decrease with decreasing $M_n$, both intrinsically\textsuperscript{5} and as a result of increased mixing with the low-$T_g$ components (reduced $\chi N$). Working within these constraints, two linear pentablock copolymers were synthesized with C block $M_n \geq 5 \, kg/mol$ and total $M_n = 150 \, kg/mol$. The synthetic details and resulting molecular characteristics are described below.
Star-shaped block copolymers, often referred to as radial polymers in the context of TPEs, are also studied as a means of further improving the mechanical performance. Changing from a linear to a star architecture (generically denoted \((A\-B)_n\), where the B blocks are connected to a central core) also has implications for the phase behavior. Theory\textsuperscript{19,20} predicts that the phase envelope (order-disorder transition) shifts to lower arm molecular weight as the number of arms increases (i.e., the ordered state is stabilized), but that the dependence of the ODT on \(n\) is weak, a point which is corroborated by experiments.\textsuperscript{21,22} Thus, a single, judicious choice of block lengths should yield single-phase melts in both the linear and star block polymers.

4.3 Synthesis of Block Copolymer Thermoplastic Elastomers

This section details the synthetic strategy for both linear and star block copolymer TPEs. The approach, outlined in Figure 4.2, consists of three steps: (1) sequential anionic polymerization, (2) chlorosilane coupling, and (3) catalytic hydrogenation. Living di- or triblock copolymer “arms” were prepared by sequential anionic polymerization of butadiene (B), styrene (S), and isoprene (I). The living arms were coupled with either a difunctional or a hexafunctional chlorosilane to afford precisely-defined, symmetric linear or 6-arm star block polymers, respectively. Finally, the polymers were catalytically hydrogenated. Specific considerations pertinent to the synthesis of block copolymer TPEs are covered here.
**Figure 4.2.** Synthetic scheme for preparing linear and star block copolymer TPEs. R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> can represent a variety of groups including polymer arms; \( n \) is either 2 or 6. Only the 1,4 structures of the polydiienes are shown for clarity.

Polymers are identified by the block sequence of the arm enclosed in parentheses followed by a subscript denoting the number of arms. Block copolymers with both semicrystalline E blocks and glassy C blocks are further followed by a dash and number (1 or 2) which denotes the ratio of the weight fractions of the E block to that of the C block. For example, (E-C-EP)<sub>2</sub>-1 and (E-C-EP)<sub>E</sub><sub>6</sub>-1 are linear and 6-arm star block copolymers, respectively, with \( w_E/w_C = 1 \). The subscript E in (E-C-EP)<sub>E</sub><sub>6</sub>-1, indicates that a few units of B were added to the living arm prior to coupling; the reason for this modification will be explained below.
4.3.1 Block Copolymer Characterization

Preparation of block copolymers by anionic polymerization of butadiene, styrene, and isoprene is well established; nonetheless, the process required some optimization. Before discussing these details, the characterization of the unsaturated precursor block copolymers must be discussed. Aliquots were taken after each polymerization step for characterization. Polymers were characterized using two techniques: the composition was determined by $^1$H NMR spectroscopy and the molecular weight and distribution were characterized by GPC.

Figure 4.3 shows representative $^1$H NMR spectra of a B-S diblock and a (B-S-I)$_2$ pentablock. Spectra were collected in 1,4-dioxane-$d_8$ to avoid overlap with the olefinic and aromatic peaks used to determine the composition. The mole fraction of each type of mer unit was calculated by integrating the appropriate region of the spectrum. The 1,2 content in the B block was determined from the B-S diblock spectrum to avoid overlap with the I block peaks. The B block synthesis (step 1a in Figure 4.2) was conducted in pure cyclohexane in all cases to minimize the 1,2 content of the B block, thus maximizing the crystallinity and melting point of the eventual E block. In cyclohexane the 1,2 content was determined to be 7.6–7.9%, corresponding to approximately 20 ethyl branches/1000 backbone carbons in the hydrogenated product. The 1,2 content in the I block was negligible, and the 3,4 content was 7.2% on average.
Figure 4.3. $^1$H NMR spectra of B-S diblock (lower) and (B-S-I)$_2$ pentablock (upper) collected in 1,4-dixoane-d$_8$ showing an expanded view of the aromatic and olefinic regions used to calculate the composition.

Molecular weights and dispersities ($D$) were calculated from the GPC traces using the differential refractive index (dRI) data calibrated with narrow distribution polystyrene standards. The apparent “polystyrene-equivalent” molecular weight ($M_{S\text{-eq}}$)—i.e. the molecular weight of a PS homopolymer with the same elution time as the polymer in question—can be converted to the true molecular weight ($M_r$) using the appropriate hydrodynamic equivalence ratio ($r$).28 The $r$ factors for each block (Table 4.2) were determined by measuring the absolute molecular weight of narrow-distribution homopolymers by light scattering (using the specific refractive index increments ($dn/dc$) in Table 4.2).
Table 4.2. Parameters for GPC Analysis

<table>
<thead>
<tr>
<th>Polymer</th>
<th>dn/dc (mL/g)</th>
<th>r</th>
<th>$\varepsilon_{254nm}$ mL/(mg cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.1251</td>
<td>1.96</td>
<td>0.005</td>
</tr>
<tr>
<td>S</td>
<td>0.1890</td>
<td>1</td>
<td>1.525</td>
</tr>
<tr>
<td>I</td>
<td>0.1302</td>
<td>1.64</td>
<td>--</td>
</tr>
</tbody>
</table>

Linear block copolymer samples were analyzed using combined $r$ factors and $dn/dc$ values calculated from the homopolymer values and the weight fractions ($w_i$) determined by $^1$H NMR spectroscopy. The S-eq molecular weight for a generic block copolymer ($M_{BCP,S-eq}$) is equal to $M_{BCP,r}$ multiplied by the sum of the weight fraction times the $r$ for each block,\(^{28-30}\) provided the GPC mobile phase is a good solvent for each block, as is the case here. The true block molecular weights of a generic ABC triblock copolymer can then be determined from the first, second, and third block aliquots using equations [4.3–5]. Recall that $r$ factor analysis applies to $M_n$; true weight-average molecular weights where calculated by $M_{w,r} = DM_{n,r}$.

Additionally, the $r$ factors determined for linear polymers cannot be applied to star polymers.

$$M_{A,r} = M_{A,S-eq} / r_A \quad [4.3]$$

$$M_{B,r} = [M_{AB,S-eq} - M_{A,S-eq}] / r_B \quad [4.4]$$

$$M_{C,r} = [M_{ABC,S-eq} - M_{AB,S-eq}] / r_C \quad [4.5]$$

Representative GPC traces, with the $r$ factor corrections applied, are shown in Figure 4.4. The traces have been normalized to a constant total area. Each polymerization produced a narrow, monomodal product ($D_B = 1.06$, $D_{B,S} = 1.09$, and $D_{B,S,I} = 1.04$). Block copolymers show minimal termination of the previous blocks. The distributions of the B-S diblock and the coupled (B-S-I)$_2$ pentablocks will be addressed in further detail below.
Figure 4.4. Normalized GPC traces following each step of the synthesis of \((E-C-EP)_{2-2}\) with elution time (a) and \(M_r\) (b) plotted on the abscissa.
True $M_w$ values for the linear and star block copolymers were determined directly from on-line light scattering ($M_{LS}$). The LS data were analyzed in ASTRA 6 (provided with the Wyatt system) using weight-fraction-weighted $dn/dc$ values. Molecular weights of constituent blocks were thus calculated by:

$$M_{B,LS} = M_{AB,LS} - M_{A,LS}$$  \[4.6\]

$$M_{C,LS} = M_{ABC,LS} - M_{AB,LS}$$  \[4.7\]

LS analysis was also used to determine the average number of arms in the coupled linear and star polymers ($n$):

$$n = M_{LS,star} / M_{LS,arm}$$  \[4.8\]

where $M_{LS,star}$ and $M_{LS,arm}$ correspond to the star and the arm measured prior to coupling, respectively.

The true $M_w$ values for the individual blocks in each block copolymer, calculated by both $r$ factor and LS analyses, are given in Table 4.3. The average discrepancy between the $r$ factor and LS calculations for the I-containing diblocks and triblocks was 1.4% with a maximum of 3%. The PI block molecular weights calculated from either Equations [4.3-4.5] or [4.6] and [4.7] agreed within 1.5% on average with a maximum discrepancy of 4% and no systematic bias. In the case of the B and S blocks $M_{LS}$ is systematically smaller than $M_{w,true}$ (by an average of 9% for B and 8% for S). This is attributed to the fact that a “universal” value of $dn/dc$ was used for each block irrespective of block length; in reality, $dn/dc$ decreases with decreasing $M_n$ for the polymers and molecular weights of interest.\(^{32-34}\) For a truly monodisperse sample, the measured value of $M_{LS}$ is inversely proportional to the value of $dn/dc$ used in the analysis, since $M_{LS} \sim [c (dn/dc)^2]^{-1}$ and $c \sim (dn/dc)^{-1}$. Thus, an erroneously large $dn/dc$ would lead to an underestimation
of $M_{LS}$ for the nearly-monodisperse samples in question. On the other hand, the $r$ factors depend on the validity of the assumption that Mark-Houwink-Sakurada exponents for the different polymers are equal in THF, which is expected to introduce comparatively less error in this molecular weight range.\textsuperscript{28,34}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{w,,r}$\textsuperscript{a} (kg/mol)</th>
<th>$M_{LS}$ (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>S</td>
</tr>
<tr>
<td>(E-EP)$_2$</td>
<td>15.6</td>
<td>56.6</td>
</tr>
<tr>
<td>(E-EP)$_6$</td>
<td>17.1</td>
<td>59.7</td>
</tr>
<tr>
<td>(E-C-EP)$_2$-2</td>
<td>11.7</td>
<td>7.2</td>
</tr>
<tr>
<td>(E-C-EP)$_2$-1</td>
<td>8.1</td>
<td>9.4</td>
</tr>
<tr>
<td>(E-C-EP)$_6$-1</td>
<td>8.7</td>
<td>9.8</td>
</tr>
<tr>
<td>(C-EP)$_2$</td>
<td>14.7\textsuperscript{b}</td>
<td>60.6\textsuperscript{b}</td>
</tr>
<tr>
<td>(C-EP)$_6$</td>
<td>14.7</td>
<td>56.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$M_{w,,r} = DM_{n,,r}$ by GPC with dRI detection, \textsuperscript{b}calculated from GPC of the S-I diblock and $w_S$ from $^1$H NMR.

The molecular characteristics determined by $^1$H NMR and GPC for the unsaturated precursors of the block copolymer TPEs are presented in Table 4.4. Linear and star block copolymers are included. The E and C weight fractions have been computed from the corresponding B and S weight fractions measured by $^1$H NMR by accounting for the addition of hydrogen atoms during hydrogenation. The predicted segregation strength between pairs of hydrogenated blocks in (E-EP)$_2$, (E-C-EP)$_2$-2, (E-C-EP)$_2$-1, and (C-EP)$_2$ have been calculated and are plotted on the phase diagram in Figure 4.1.
Table 4.4. Molecular Characteristics of Unsaturated TPE Precursors

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{LS}$ (kg/mol)</th>
<th>$M_{n,r}$ (kg/mol)</th>
<th>$D$</th>
<th>$n^a$</th>
<th>1,2-B (mol%)</th>
<th>branch content$^b$</th>
<th>3,4-I (mol%)</th>
<th>$w_E^c$</th>
<th>$w_C^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-EP)$_2$</td>
<td>137</td>
<td>132</td>
<td>1.07</td>
<td>1.95</td>
<td>7.9</td>
<td>21</td>
<td>7.2</td>
<td>0.20</td>
<td>--</td>
</tr>
<tr>
<td>(E-EP$_E$)$_6$</td>
<td>478</td>
<td>--</td>
<td>1.15</td>
<td>6.13$^d$</td>
<td>7.6</td>
<td>20</td>
<td>6.9</td>
<td>0.19</td>
<td>--</td>
</tr>
<tr>
<td>(E-C-EP)$_2$-2</td>
<td>164</td>
<td>153</td>
<td>1.08</td>
<td>1.95</td>
<td>7.8</td>
<td>20</td>
<td>7.1</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>(E-C-EP)$_2$-1</td>
<td>158</td>
<td>154</td>
<td>1.07</td>
<td>1.89$^e$</td>
<td>7.7</td>
<td>20</td>
<td>7.7</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>(E-C-EP$_E$)$_6$-1</td>
<td>500</td>
<td>--</td>
<td>1.13</td>
<td>5.86</td>
<td>7.8</td>
<td>20</td>
<td>7.3</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>(C-EP)$_2$</td>
<td>144</td>
<td>138</td>
<td>1.08</td>
<td>1.95</td>
<td>--</td>
<td>--</td>
<td>7.1</td>
<td>--</td>
<td>0.20</td>
</tr>
<tr>
<td>(C-EP$_E$)$_6$</td>
<td>427</td>
<td>--</td>
<td>1.21</td>
<td>5.76</td>
<td>--</td>
<td>--</td>
<td>7.4</td>
<td>--</td>
<td>0.19</td>
</tr>
</tbody>
</table>

$^a$Includes uncoupled arm, $^b$ethyl branches per 1000 backbone carbons, $^c$after saturation, $^d$a small high molecular-weight shoulder in the coupled polymer leads to $n > 6$, $^eM_{w,arm}$ determined on a partially coupled sample.

4.3.2 Polybutadienyllithium Crossover to Styrene

En route to the materials with composite crystalline-glassy physical cross-links, GPC analysis revealed that the dispersity of B-S diblocks prepared in cyclohexane (Figure 4.5a) was significantly larger than that of the B blocks. The inferred broad dispersity of the S blocks was attributed to the slow rate of crossover from polybutadienyllithium to styrene compared to the rate of styrene propagation.$^{35}$ The need for short glassy blocks exacerbates this issue, and in the worst-case scenario may lead to a population of chains with little or no S block.
Figure 4.5. GPC traces (dashed) and styrene content (solid) of B-S diblock copolymers synthesized in neat cyclohexane (a) and 1:1 (v/v) cyclohexane/benzene (b). Open circle and error bars indicate average styrene content and standard deviation, respectively. GPC traces are normalized to a constant area and plotted with the same vertical scale to facilitate comparison. In both cases the target block molecular weights were 10 kg/mol and 5 kg/mol for B and S, respectively.
To ameliorate this issue, it was necessary to increase the rate of crossover relative to styrene propagation. The crossover rate can be increased by increasing the polarity of the solvent;\textsuperscript{35} however, the common polar modifiers (ethers, amines, etc.) are not suitable since they would drastically increase the vinyl content of the I block, raising the $T_g$ of the hydrogenated rubbery block\textsuperscript{36} and detracting from the elastomeric performance. Instead, aromatic solvents were tested as cosolvents to enhance the rate of crossover while preserving the high 1,4 microstructure\textsuperscript{37} of the I block. The cosolvent (1:1 by volume to cyclohexane) was vacuum-transferred into the reactor after polymerizing the B block to completion in pure cyclohexane to minimize 1,2-addition (between steps 1a and 1b in Figure 4.2). A test polymerization of B in 1:1 (v/v) cyclohexane/benzene had a 1,2 content of 9.2 mol\%, corresponding to 24 branches/1000 C if hydrogenated, which would be expected to reduce the PE melting point by approximately 5 °C.\textsuperscript{3,4} Using toluene or ethylbenzene as the cosolvent was successful in reducing $D$ of the S block, but led to chain transfer during the I block polymerization (via $\alpha$-hydrogen abstraction).\textsuperscript{38} Benzene improved the crossover and showed no evidence of chain transfer (Figure 4.5b), and was thus used in all subsequent polymerizations. Figure 4.5 shows that the addition of benzene narrows the molecular weight distribution of the diblock (in neat cyclohexane $D_{B,S} = 1.11$, while in 1:1 cyclohexane/benzene $D_{B,S} = 1.09$); the improvement is partially obscured by the narrow-distribution B block which constitutes two-thirds of the mass.

The distribution of the PS block was assessed in further detail by comparing the UV absorbance and differential refractive index ($\Delta n$) signals from the GPC traces. The UV absorbance ($A_{UV}$) measured as a function of elution time ($t_v$) can be related to the mass concentrations ($c_i$) of each component by:

$$\frac{A_{UV}(t_v)}{L} = c_B(t_v) \varepsilon_B + c_S(t_v) \varepsilon_S$$  \hspace{1cm} [4.8]
where $\varepsilon_i$ is the UV extinction coefficient of component $i$ and $L = 1$ cm is the UV path length. Similarly, the dRI signal can be written as:

$$\Delta n(t_v) = c_B(t_v) \left( \frac{dn}{dc} \right)_B + c_S(t_v) \left( \frac{dn}{dc} \right)_S$$  \[4.9\]

where $(dn/dc)_i$ is the specific refractive index increment of component $i$. Values of $dn/dc$ and $\varepsilon$ are listed in Table 4.2; since $\varepsilon_S \gg \varepsilon_B$, the contribution of B to the UV signal was neglected. Equations [4.8] and [4.9] were solved for $c_B$ and $c_S$ at each $t_v$ and converted to weight fractions ($w_i$) using ASTRA 6. The results are shown in Figure 4.5 (solid curves). The average $w_S$ was in good agreement with the monomer charges in both cases. The diblock synthesized in pure cyclohexane had $w_S = 0.31 \pm 0.13$ (one standard deviation) with $w_{S,min} = 0.15$ and $w_{S,max} = 0.49$. The diblock synthesized in 1/1 v/v cyclohexane/benzene had $w_S = 0.30 \pm 0.09$ with $w_{S,min} = 0.19$ and $w_{S,max} = 0.44$; adding 50 vol% benzene reduces the standard deviation and range in S content by 30% and 25%, respectively. For consistency, all polymerizations—except for the initial B blocks—were conducted in 1:1 (v/v) cyclohexane/benzene regardless of the block sequence. The 3,4 content of I blocks prepared in this solvent mixture was a modest 6.9–7.7%.
4.3.3 Chlorosilane Coupling

The approach of coupling the living di- or triblock copolymer via termination with multifunctional chlorosilanes provides several advantages. Though the linear block copolymers could be prepared by sequential monomer additions, chlorosilane coupling reduces the number of monomer additions and polymerization steps and ensures that the resulting block copolymers are symmetric. Moreover, chlorosilane coupling of living anionic polymers remains one of the most versatile and reliable methods for synthesizing star block copolymers.

While this method is widely practiced, it does suffer from some drawbacks. The coupling reaction is slow in the hydrocarbon solvents commonly used for anionic polymerization. In hydrocarbon solvents the reaction between carbanions and chlorosilane coupling agents can take days or even weeks to go to completion; the reaction slows down precipitously as the number of arms increases due to increased steric hindrance. The rate and efficiency of coupling are also sensitive functions of the steric environment at the core of the star. Such lengthy reaction times necessitate the rigorous exclusion of impurities to levels achievable only by glassblowing techniques. Due, at least in part, to the sluggish addition of arms, precise stoichiometric coupling is exceedingly difficult. In practice, a stoichiometric deficiency of coupling agent is commonly added to prevent the formation of stars with intermediate functionality yielding a mixture of stars with the desired functionality and still-living arms. After the remaining arms have been terminated, the mixture is typically fractionated to isolate the star polymer. A route to rapid and complete coupling is thus sought to avoid these difficult and time-consuming procedures.

It has been known for some time that the propagation rate of anionic polymerization increases sharply with the addition of polar additives, such as amines and ethers. This effect has
been attributed to changes in the bonding character between the carbanion and the counterion, and the aggregation state of the ionic living ends in solution.\textsuperscript{56} A similar effect has been suggested for the rate of chlorosilane coupling in the presence of polar additives.\textsuperscript{48,49,57} However, there are many polar additives to choose from, and the rate increase has not been quantified. In light of the potential benefits, the effect of two representative polar additives on the rate of chlorosilane coupling was investigated in detail. High 1,4-polyisoprenyllithium (I-Li, $M_w \approx 8$ kg/mol), prepared in cyclohexane, was coupled with dimethyldichlorosilane (DMDCS) in the presence of five equivalents of triethylamine (TEA) or tetrahydrofuran (THF) to Li. While both additives increased the rate of coupling compared to the neat cyclohexane case (Figure 4.6), THF was markedly more successful. In the presence of just five equivalents of THF the coupling reaction was nearly instantaneous. This tremendous improvement in the coupling rate, and consequently in the coupling efficiency at practical reaction times (hours or less), enables an important change in synthetic procedure.
Figure 4.6. GPC traces of coupling living I-Li with DMDCS in cyclohexane ($M_{w,arm} = 8.4$ kg/mol) (a), with five equivalents of triethylamine to lithium ($M_{w,arm} = 7.8$ kg/mol) (b), and with five equivalents of tetrahydrofuran to lithium ($M_{w,arm} = 9.1$ kg/mol) (c).
Instead of the usual approach where a (sometimes large) deficiency of coupling agent is employed to ensure that the coupled polymer has the desired functionality—thereby necessitating tedious fractionation—the addition of THF enables near-stoichiometric coupling via a visual titration method. While polyisoprenyllithium (I-Li) is nearly colorless in apolar hydrocarbon media, in the presence of even small quantities of THF the living ends produces a distinct yellow color, the intensity of which depends on the concentrations of both I-Li and THF. When DMDCS is added to the living polymerization as a dilute solution in THF—to facilitate the precise addition of small volumes of coupling agent—the initial addition of coupling agent solution causes a faint yellow color to emerge. Adding more coupling agent solution causes the color intensity to go through a maximum as the THF concentration increases but the living ends are consumed by coupling. Further dropwise addition of coupling agent solution causes the yellow color to wane and ultimately disappear, indicating that coupling has finished. Since the reaction is fast when coupling I-Li with DMDCS, precise knowledge of the living end concentration is not required to achieve near-stoichiometric coupling. Thus, discrepancies in living end concentration due to initiator activity or adventitious termination do not diminish the coupling efficiency. This approach is also applicable to polybutadienyllithium and polystyryllithium living ends, which similarly undergo color changes with changes in solvent polarity.

Given the success with DMDCS, the coupling rate between I-Li ($M_{w,arm} \approx 84 \text{ kg/mol}$, prepared in cyclohexane) and 2,2,4,4,6,6-hexachloro-2,4,6-trisilahpane ($x = 6$, denoted $\text{Si}_3\text{Cl}_{3x2}$) in the presence of THF was investigated. The coupling agent was added as a 0.02 M solution in either cyclohexane or THF (corresponding to THF:Li = 100:1 at the endpoint of coupling) over the course of a few minutes. Figure 4.7 shows the evolution of the molecular
weight distributions measured by GPC. The increase in hydrodynamic volume diminishes with the addition of each successive arm, making high-functionality stars of different \( n \) unresolvable by GPC. Two peaks—uncoupled arm eluting near 13 minutes and stars \( (n \geq 3) \) at shorter elution times—are clearly resolved in all traces, as shown in Figure 4.7. The coupling reaction was tracked using two metrics: the weight-average functionality \( (n) \), and the coupling efficiency, measured by the weight fraction of star \( (w_{\text{star}}) \) computed by integrating the normalized dRI signal. Figure 4.8 shows the progression of \( n \) and \( w_{\text{star}} \) over the course of the coupling reaction.

In neat cyclohexane approximately half of the mass was converted to 3-arm star in the first five minutes; the fourth and fifth arms were added within 48 hours \( (n = 5.0 \text{ and } w_{\text{star}} = 0.80) \). The addition of the sixth arm was considerably slower; after one month only a modest increase in coupling was observed \( (n = 5.2 \text{ and } w_{\text{star}} = 0.82) \). These findings are consistent with previous reports on the coupling kinetics of PI-Li living ends with 1,2-bis(trichlorosilyl)ethane in benzene to make 6-arm stars.\(^{41,42}\) After one month, 100 eq. of THF to Li was added to facilitate the coupling of any remaining living I-Li. Only a small amount of additional coupling was observed \( (n = 5.3 \text{ and } w_{\text{star}} = 0.84) \), indicating that the majority of the remaining uncoupled arm had been adventitiously terminated, despite having been stored in a sealed reactor inside a glovebox with <0.1 ppm of oxygen and moisture.
Figure 4.7. Selected GPC traces over the course of the coupling reaction of I-Li with Si$_3$Cl$_3$×2 in neat cyclohexane ($M_{w,arm} = 85$ kg/mol) (a) and with THF:Li = 100 ($M_{w,arm} = 83$ kg/mol) (b) at room temperature. The differential refractive index signal of each trace has been normalized to a constant total area.
Figure 4.8. The weight-average functionality (a) and star weight fraction (b) of I-Li coupled with $\text{Si}_3\text{Cl}_{3\times 2}$ in neat cyclohexane ($\text{THF:Li} = 0$, $M_{w,\text{arm}} = 85 \text{ kg/mol}$) and with $\text{THF:Li} = 100$ ($M_{w,\text{arm}} = 83 \text{ kg/mol}$) at room temperature plotted versus reaction time. Lines are guides to the eye. THF (100 eq.) was added to the reaction in neat cyclohexane after 30 days to assess the viability of the remaining arms. The final functionality and star weight fraction obtained after adding THF are indicated by the filled diamonds.
In contrast, the addition of 100 eq. THF concurrently with the coupling agent produced 80 wt% 5-arm star in minutes and the addition of the sixth arm was complete within three hours. As with DMDCS, the presence of a small amount of THF drastically improved both the functionality \((n = 6.0)\) and coupling efficiency \(w_{\text{star}} = 0.95\) of the final product. Based on the results in neat cyclohexane, using THF is not only convenient but necessary with conventional reactors (not sealed by glassblowing), otherwise adventitious termination would consume the living ends prior to complete coupling. Although the coupling reaction was not instantaneous, making complete coupling by dropwise titration infeasible, the color of the living ends still proves useful in achieving high coupling efficiency. Adding the coupling agent solution until the reaction is nearly, but not completely, colorless allows the stoichiometric deficiency of coupling agent, needed to avoid forming stars of intermediate functionality, to be minimized without precise knowledge of the living end concentration. Consequently, the fraction of uncoupled arms can be reduced significantly compared to similar reports of stars prepared using glassblowing techniques in the absence of THF.\(^{39,40,53-55,58}\)

The procedure just described was used to prepare the 6-arm star block copolymer TPEs studied in this work. The procedure consistently yielded approximately 95% coupled material. Studies on S-I-S/S-I and S-B-S/S-B blends have elucidated the impact of residual arm material on the mechanical properties of triblock copolymer TPEs.\(^{59-62}\) The modulus is minimally affected by uncoupled material\(^{62}\) so long as the uncoupled rubbery block \(M_n\) is sufficiently above the entanglement molecular weight (as is the case in this work, \(M_e \approx 1.5 \text{ kg/mol}\)\(^7\) for EP). The ultimate strength scales essentially linearly with the coupled fraction.\(^{60,62}\) Although the strain at break may increase with diblock content\(^{61}\), the majority of this additional deformation is likely
unrecoverable. Thus, the ca. 5% residual arm should minimally affect the mechanical performance, and fractionation was deemed unnecessary.

4.3.4 Catalytic Hydrogenation

Catalytic hydrogenation is necessary to produce semicrystalline E blocks and improve the thermo-oxidative stability of the rubbery block. The efforts described above to minimize the amount of uncoupled material during synthesis are effective only insofar as the well-defined architecture can be maintained through the hydrogenation process. In particular, the stability of the Si-C bonds at the core of the coupled polymers during hydrogenation is a potential concern. There are relatively few published reports\textsuperscript{55,63-68} on the catalytic hydrogenation of chlorosilane-coupled star polymers. In cases where the molecular weight distribution was characterized after hydrogenation, degradation of the star architecture, evidently by Si-C bond scission at the core, was observed.\textsuperscript{63,64} This was remedied by post-hydrogenation fractionation; however, this is a painstaking process since stars of similar functionality are difficult to separate. Additionally, stars with semicrystalline components, such as hydrogenated high 1,4-polybutadiene,\textsuperscript{55,66-68} are not amenable to fractionation at room temperature.

Four hydrogenation catalysts, representing a range of activity and selectivity, were used to test the stability of the polymers prepared as described in the preceding sections. Test hydrogenations were conducted on a DMDCS-coupled linear block copolymer with S-I arms (abbreviated (S-I)$_2$, see Table 4.5 for characterization). Two supported catalysts, Pd/CaCO$_3$ and Pt–Re/SiO$_2$, were used to completely hydrogenate both olefinic and aromatic unsaturation. The Pt–Re/SiO$_2$ catalyst was designed to efficiently hydrogenate the S, and is thus significantly more active than Pd/CaCO$_3$.\textsuperscript{5,69-71} Two unsupported catalysts, which preserve the aromatic rings in the
S blocks, were also studied: a Ni–Al (Ziegler-type) catalyst, which offers tunable selectivity but limited activity\textsuperscript{72-74} and a homogeneous catalyst, Ru(CO)ClH(PPh\textsubscript{3})\textsubscript{3}, chosen for its demonstrated activity\textsuperscript{75,76} and commercial availability.

Table 4.5. Molecular Characteristics of Coupled Polymers\textsuperscript{a} and Hydrogenation Results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M\textsubscript{LS,arm} (kg/mol)</th>
<th>w\textsubscript{S}</th>
<th>n</th>
<th>Hydrogenation Catalyst</th>
<th>T (°C)</th>
<th>w\textsubscript{d} \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Linear Polymers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S-I)\textsubscript{2}</td>
<td>67</td>
<td>0.19</td>
<td>2.0</td>
<td>Pt–Re/SiO\textsubscript{2}</td>
<td>170</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>170</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>120</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ni–Al</td>
<td>80</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ru(CO)ClH(PPh\textsubscript{3})\textsubscript{3}</td>
<td>160</td>
<td>0.07\textsuperscript{c}</td>
</tr>
<tr>
<td><strong>4-arm Stars</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I\textsubscript{4}-L</td>
<td>9.1</td>
<td>0</td>
<td>3.8</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>100</td>
<td>0.36</td>
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<tr>
<td>I\textsubscript{4}-H</td>
<td>78</td>
<td>0</td>
<td>3.9</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>100</td>
<td>0.30</td>
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<tr>
<td>I\textsubscript{2x2}</td>
<td>87</td>
<td>0</td>
<td>3.9</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>100</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>6-arm Stars</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I\textsubscript{6}-a</td>
<td>72</td>
<td>0</td>
<td>6.0</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>100</td>
<td>0.04</td>
</tr>
<tr>
<td>I\textsubscript{6}-b</td>
<td>83</td>
<td>0</td>
<td>6.0</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>120</td>
<td>0.14</td>
</tr>
<tr>
<td>(S-I)\textsubscript{6}</td>
<td>68</td>
<td>0.19</td>
<td>6.0</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>120</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>135</td>
<td>0.16</td>
</tr>
<tr>
<td>(S-I\textsubscript{B})\textsubscript{6}</td>
<td>71</td>
<td>0.19</td>
<td>6.0</td>
<td>Pd/CaCO\textsubscript{3}</td>
<td>120</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Prior to hydrogenation, \textsuperscript{b}weight fraction degraded at the end of hydrogenation, \textsuperscript{c}1,4-I saturation limited to 73%.
Figure 4.9 shows the GPC traces of (S-I)$_2$ after hydrogenation with each of the four catalysts, along with that of the precursor polymer. The elution times have been shifted to account for changes in the hydrodynamic volume upon hydrogenation, facilitating comparison. The severity of degradation was quantified through the weight fraction of the coupled polymer which degraded to uncoupled arm:

$$w_d = \frac{w_{arm} - w_{arm,0}}{1 - w_{arm,0}}$$

[4.10]

where $w_{arm} = 1 - w_{star}$ is measured by integrating the dRI traces and $w_{arm,0}$ is measured before hydrogenation. The results are summarized in Table 4.5. At 170 °C, both supported catalysts produced a large amount of scission; Pt–Re/SiO$_2$ degraded nearly half of the coupled polymer while Pd/CaCO$_3$ degraded about a third of the coupled polymer. In both cases, hydrogenation was complete in approximately 8 hours (notwithstanding the factor-of-10 lower catalyst loading for Pt–Re/SiO$_2$). Reducing the temperature from 170 °C to 120 °C with Pd/CaCO$_3$ tripled the reaction time but reduced the degree of scission by more than a factor of three, a point which will be revisited below.
Figure 4.9. GPC traces of (S-I)\textsubscript{2} before and after catalytic hydrogenation with two supported (a) and two unsupported (b) hydrogenation catalysts.
The Ni–Al catalyst was prepared using a Ni–Al ratio known to be selective for polydienes in PS-polydiene block copolymers.\textsuperscript{14,15} Four catalyst additions at 80 °C yielded >99% saturation of the 1,4-I and approximately 20% degradation. Given that the selectivity of the Ni–Al catalyst is a sensitive function of the metal ratio\textsuperscript{72,73} it may be possible to reduce the scission by adjusting the Ni to Al ratio; however, it seems unlikely that degradation could be eliminated without greatly reducing the activity or selectivity. In a separate test, additional catalyst charges (10 total) did not lead to further degradation.

The organometallic catalyst Ru(CO)ClH(PPh\textsubscript{3})\textsubscript{3} was also tested, but was unable to completely saturate the I block. The 1,4-I and 3,4-I were 73% and 95% saturated, as measured by \textsuperscript{1}H NMR, indicating that the steric hindrance of the trisubstituted carbon-carbon double bond of the 1,4-I units is apparently enough to hinder coordination with the catalyst. However, the relatively small amount of degradation (Figure 4.9) and demonstrated activity of related catalysts\textsuperscript{77} for the hydrogenation of butadiene repeat units may make them attractive for hydrogenating chlorosilane-coupled polybutadiene stars. With all four catalysts, little or no additional scission was observed once the maximal saturation was reached, indicating that the degradation and hydrogenation are inextricably linked and that the elevated temperatures and vigorous stirring are not major contributors to the scission.

Though it may be possible to further optimize the hydrogenation conditions using Ni–Al or Ru(CO)ClH(PPh\textsubscript{3})\textsubscript{3}, the supported catalysts, which are capable of fully hydrogenating S blocks, are preferred. In the context of TPEs with composite crystalline-glassy hard domains, fully hydrogenated C glassy blocks have a few advantages over the aromatic S blocks: (1) C has a lower $\chi$ against E\textsuperscript{14} and EP, permitting access to disordered melts at higher molecular weights,
and (2) the $T_g$ of C is $\approx 45$ °C higher than that of S. Of the two catalysts, Pd/CaCO$_3$ produces less degradation at comparable conditions, and was thus studied in further detail.

The stability of chlorosilane-coupled star polymers was studied using 6-arm stars (coupled with Si$_3$Cl$_{3\times2}$) with either I or (S-I) arms, denoted I$_6$ and (S-I)$_6$. The molecular characteristics of each of the star polymers discussed in this section before and after hydrogenation are presented in Table 4.5. The decoupling between scission and the time required for hydrogenation is clearly illustrated in Figure 4.10. Figure 4.10a shows the fractional saturation of 1,4-I units as a function of hydrogenation time. Incorporating the S block into the arms significantly reduces the rate of hydrogenation of all blocks; at 120 °C I$_6$-b reaches 99% saturation in 8 hours while (S-I)$_6$ takes 76 hours to reach the same mark. The fraction of star degraded to arm ($w_d$) was quantified over the course of the hydrogenation reaction. Despite the nearly 10-fold difference in reaction time, the degree of scission in the two polymers is similar, as illustrated in Figure 4.10b. As noted above with (S-I)$_2$, subjecting I$_6$-b to the hydrogenation conditions after saturation was complete did not appreciably increase the degree of degradation.
Figure 4.10. Fractional saturation of the 1,4-I units, calculated by $^1$H NMR, as a function of hydrogenation time (a) and the fraction of star which was degraded to arm ($w_d$) as a function of fractional 1,4-I saturation (b) for $I_6$-$b$, (S-I)$_6$, and (S-$I_B$)$_6$ 6-arm stars hydrogenated over Pd/CaCO$_3$ at 120 °C. Lines are guides to the eye.
The reaction temperature also impacted the degree of degradation for the 6-arm stars, as was observed for (S-I)$_2$, providing further evidence that the scission reaction is a catalytically activated process. When hydrogenated at 100 °C, I$_6$-a reached complete saturation quickly (<4 hours, the first data point taken) and showed significantly less degradation than I$_6$-b, which was hydrogenated at 120 °C (Figure 4.11). The same trend was observed for (S-I)$_6$, though the reaction times required to reach complete saturation were much longer. At 120 °C, (S-I)$_6$ reached 99% saturation after 76 hours of hydrogenation. Increasing the temperature by 15 °C halved the reaction time but increased the final $w_d$ by nearly 50% (Figure 4.12).

![Figure 4.11. GPC traces of I$_6$-a (a) and I$_6$-b (b) before and after hydrogenation.](image)
Figure 4.12. GPC traces of (S-I)$_6$ (a) and (S-I$_B$)$_6$ (b) before and after hydrogenation.

Given that the degradation reaction appears to be catalytically activated, the decreasing rate of degradation with increasing degree of saturation may be attributed to the decreasing affinity of the polymer for the catalyst. Adsorption of polymer chains onto the active sites of the catalysts is driven by the favorable enthalpic interactions between unsaturated moieties in the polymer and the metal.$^{70,78}$ When the arms are saturated, the polymer—and thus the core—no longer interact strongly with catalyst, preventing further degradation. While it might be possible to reduce degradation by tuning the hydrogenation conditions (catalyst and temperature), the relationship between degradation and hydrogenation restricts this approach to polymers which hydrogenate quickly (e.g., polydienes). The mild conditions necessary to reduce degradation lead to intractably long reaction times when stars contain a component which hydrogenates slowly, such as S,$^{70,78}$ so alternative routes for preserving the architecture are required.

Given the demonstrated$^{39,48-51}$ importance of the core sterics for the coupling reaction, the stability of the Si-C bonds during hydrogenation might also be expected to depend on the steric environment at the core of the star. If so, then using coupling agents with densely packed
functional groups or accommodating arms with bulky substituents, which create steric strain at the core, would potentially make the star more susceptible to degradation. It follows that degradation of complex architectures during hydrogenation might be reduced through careful choice of the coupling agent. This hypothesis was tested using PI stars coupled with silicon tetrachloride (SiCl\textsubscript{4}) and bis(methyldichlorosilyl)ethane (Si\textsubscript{2}Cl\textsubscript{2x2}), abbreviated PI\textsubscript{4} and PI\textsubscript{2x2}, respectively (see Table 4.5 for details). These coupling agents have the same overall functionality but different topologies; in Si\textsubscript{2}Cl\textsubscript{2x2} the Si atoms are separated by an ethyl spacer and each bears only two arms while in SiCl\textsubscript{4} all four arms are connected to a single Si atom.

Table 4.5 and Figure 4.13 show that nearly one-third of PI\textsubscript{4}-H was degraded to uncoupled arm during hydrogenation while only 7% of PI\textsubscript{2x2} reverted to arm. The comparatively large fraction of regenerated arm in hydrogenated PI\textsubscript{4} is attributed to the highly strained core.

The saturated product of I\textsubscript{4}-H primarily comprises 4-arm star and uncoupled arm. Very little 3-arm star (\(n = 3.6\) for the remaining coupled material) and almost no difunctional material (no shoulder in Figure 4.13a near 12.4 min, cf. Figure 4.13b) are evident. Thus, it appears that stars either degrade completely, down to individual arms, or not at all.
It is interesting to note that reducing the arm molecular weight by nearly an order of magnitude did not appreciably affect either the degree of degradation or the nature of the degradation products. Catalytic hydrogenation of polymers over supported metallic catalysts is a complex process which involves transport, adsorption, reaction, and desorption. It has been shown\textsuperscript{70,71} that the adsorption/desorption process depends on the overall molecular weight of the polymer chain. To probe whether this molecular weight effect is important for the extent of degradation, two SiCl$_4$-coupled I stars (I$_4$-L and I$_4$-H) with arm molecular weights differing by nearly an order of magnitude were hydrogenated over Pd/CaCO$_3$ at 100 °C. The higher molecular weight polymer (I$_4$-H) apparently showed slightly less degradation ($w_d = 0.30$) than the lower molecular weight polymer (I$_4$-L, $w_d = 0.36$), although the difference may be within the reproducibility of the experiment. Thus, arm molecular weight has little effect on degradation over the range studied.
Although PI\textsubscript{2\times2} showed less scission overall, due to the relaxed steric environment, a notable fraction of difunctional polymer was produced. There are two types of Si-C bonds in I\textsubscript{2\times2} (as is also necessarily true for stars with \(x > 4\) made by chlorosilane coupling), and thus two possible routes to a polymer molecule with \(n = 2\). Either two arms can be lost, generating two free arms and a difunctional polymer, or an internal Si-C bond (between either of the Si atoms and the ethyl spacer) can be broken, yielding two difunctional polymers. In light of the I\textsubscript{4}-H and I\textsubscript{4}-L results, the relatively high functionality of the remaining coupled material (\(n = 3.4\), including the difunctional fraction) and the appreciable fraction of uncoupled arms in hydrogenated PI\textsubscript{2\times2}, the former mechanism may be dominant. The \(\alpha,\beta\)-unsaturation may be responsible for the apparent weakness of the Si-C bonds between the coupling agent and the polymer arms. The limited reports of bond strengths in model aliphatic silanes offer some support for this hypothesis; the Si-C bond dissociation energy of the allyl group in allyltrimethylsilane is approximately 25% lower than that of a methyl group in tetramethylsilane;\textsuperscript{79} increasing alkyl chain length also reportedly weakens the Si-C bond somewhat.\textsuperscript{80} This may also contribute to the apparent increase in star stability with increasing degree of saturation during hydrogenation. Regardless of the mechanism, tuning the topology of the coupling agent is insufficient to suppress the formation of free arms and lower-functionality stars during hydrogenation of star polymers.

Up to this point only a single interior block (high 1,4-I) has been considered. The only mer unit with less steric hindrance than isoprene is butadiene.\textsuperscript{48-51} The favorable sterics of B-Li chain termini have been utilized in previous reports to facilitate chlorosilane coupling.\textsuperscript{44,47-52} Building on this success, a short run or “cap” of B units (~9 B/chain on average, determined by \textsuperscript{1}H NMR) was added to (S-I)-Li arms prior to coupling with Si\textsubscript{3}Cl\textsubscript{3\times2} to reduce the steric strain at
the core. The resulting 6-arm star (details in Table 4.5), denoted (S-I_B)_6, was subsequently hydrogenated over Pd/CaCO_3 at 120 °C. Figure 4.10 shows that although the hydrogenation kinetics are not affected by the presence of the B units at the core (all three types of repeat units hydrogenate at the rate of the slowest component, i.e., S), scission is nearly eliminated due to the reduction in steric strain. GPC traces prior to and following hydrogenation of (S-I)_6 and (S-I_B)_6 are shown in Figure 4.12; in comparison with (S-I)_6, the formation of both arms and lower-functionality coupled polymers in (S-I_B)_6 during hydrogenation is greatly suppressed.

A butadiene cap was incorporated into the arms of all of the star block copolymers studied as TPEs to minimize degradation during hydrogenation. Butadiene was vacuum transferred into the reactor (containing the living arms in an equal volume of cyclohexane and benzene) and was allowed to polymerize at room temperature (to minimize 1,2-addition) for 1.5 h before charging the coupling agent stock solution. Degradation in (E-EP_E)_6 and (E-C-EP_E)_6 could not be directly assessed, since these polymers are insoluble at room temperature; however, it is reasonable to assume that the molecular weight distributions resemble that of hydrogenated (S-I_B)_6 (Figure 4.12a) given the similarity between I_b-b and (S-I)_6 hydrogenated under the same conditions.

Incorporating a B cap clearly reduces degradation of the star architecture during hydrogenation; however, this approach is only effective if each chain receives the requisite B cap. Studies of coupling efficiencies of polydienes with different microstructures reveal that one B unit per chain may be insufficient; Cho et al. found that low 1,4-polyisoprenyllithium and polybutadienyllithium, synthesized using the polar modifier N,N',N"-tetramethylethylene diamine (TMEDA), could not be efficiently coupled with DMDCS. High 1,4-polydienyllithium, on the other hand, could be efficiently coupled when TMEDA was added.
immediately prior to coupling. It is important to note that the microstructure (i.e., 1,4-addition versus 1,2 or 3,4-addition) of the terminal diene unit is undetermined until it reacts with the coupling agent. Thus, the high coupling efficiency of high 1,4-polydienes imply that the steric constraints at the core impose a strong preference for 1,4-enchainment of the terminal monomer unit, despite the preference for 1,2 or 3,4-addition in the presence of the polar additive. The same must be true regardless of the total 1,4 content of the arm; therefore, the poor coupling efficiencies observed for high vinyl arms indicates that at a minimum the penultimate unit also contributes to the steric environment. In light of this, the B cap should be at least two units long for maximum efficacy. Moreover, the vinyl content in the B cap should be minimized. At the other extreme, the cap length should not be so long that the hydrogenated low-vinyl B cap can crystallize.

The average number of B per chain required to ensure each chain receives the minimum number of units is determined by the kinetics of the crossover reaction. The propensity of an individual chain to add a B unit depends on the identity of the chain end. The two possible reactions, crossover and B propagation, are illustrated with I-Li in Figure 4.14. While the capping approach can be extended to any arm chemistry capable of adding B units, the distribution of B cap lengths and, more importantly, the average number of B units per chain needed to ensure that each chain receives the minimum number of units, is be determined by the relative rates of crossover and B propagation. If the crossover is fast relative to B propagation, the B units adds more quickly to the chains which have not crossed over. This scenario produces a narrow cap length distribution, and complete capping can be achieved with relatively few B units per chain on average. This is clearly the preferred scenario. On the other hand, if the
crossover is slow compared to B propagation, a large number of B units per chain on average will be necessary to ensure that each chain receives the minimum number of B units.

![Possible reactions during the capping of I-Li with B.](image)

**Figure 4.14.** Possible reactions during the capping of I-Li with B.

A simple stochastic kinetic model was developed to elucidate the capping process in further detail. In the model the probability for an individual chain to add a B unit depends only on the identity of the terminal unit; as depicted in Figure 4.14, there are two possibilities. The simulation tracks the identity of the living end and the number of B units in each chain for $10^4$ independent chains. The probability that a B unit adds to a given chain during a given iteration is proportional to the appropriate rate constant—$k_{IB}$ if the living end is I-Li and $k_{BB}$ if the living end is B-Li. The dependence of the rate on the concentrations of living ends and B monomer is assumed to be independent of the identity of the living end. The probability of adding a B unit is such that the probability of adding two B units to a single chain in one iteration is vanishingly small, regardless of the identity of the chain end. The simulation is run until the desired average number of B units per chain (simply the total number of incorporated B units divided by the number of chains, denoted $<\text{B/chain}>$) is reached. The stochastic model was used to simulate the
B cap length distribution as a function of the relative rate constants. The primary quantity of interest is the fraction of chains which remain uncapped.

To simulate capping I-Li with B, the relevant rate constants were taken from the literature. The propagation rate, and by inference the crossover rate, is first-order in monomer concentration, but sub-first-order in living end concentration, [Li]. Moreover, both rates are sensitive functions of the solvent polarity and reaction temperature. In this work, [Li] = 0.5–1 mM, the solvent was either neat cyclohexane or 1:1 v/v cyclohexane/benzene, and the capping reaction was done at room temperature (20–25 °C). Rate constants were chosen from the literature to match these conditions as closely as possible. The crossover rate constant, \( k_{IB} \), was determined from the reactivity ratio \( r_I = k_{II}/k_{IB} = 0.35 \) ([Li] = 1.3 mM, in hexane, at 30 °C) and the isoprene propagation rate constant \( k_{II} = 9.67 \times 10^{-5} \, \text{s}^{-1} \) ([Li] = 0.704 mM, in hexane, at 30 °C). Using the B propagation rate constant \( k_{BB} = 0.802 \times 10^{-5} \, \text{s}^{-1} \) ([Li] = 0.683 mM, in hexane, at 20 °C), \( k_{IB}/k_{BB} = 34 \).

Remarkably, simulations with \( k_{IB}/k_{BB} = 34 \) reveal that an average of just one B/chain is enough to cap 94% of the chains, and \(<\text{B/chain}> = 2\) is sufficient to guarantee complete (>99.99%) capping, as shown in Figure 4.15. Three additional scenarios were also simulated for a generic living end A-Li: \( k_{AB}/k_{BB} = 10, k_{AB}/k_{BB} = 1, \) and \( k_{AB}/k_{BB} = 0.1 \); the results are shown in Figure 4.15. In the most favorable case, where \( k_{AB}/k_{BB} = 10, <\text{B/chain}> = 2 \) is again sufficient to cap all (>99.99%) of the chains, illustrating that although there is some uncertainty associated with the literature values of \( k_{IB} \) and \( k_{BB} \), capping I-Li with B is quite robust. When the rates of crossover and propagation are equal, \( <\text{B/chain}> = 5 \) is required to achieve an uncapped fraction of <1%. In the least favorable case, when propagation is an order of magnitude faster than the crossover, adding \( <\text{B/chain}> = 15 \) still leaves nearly 10% of the chains uncapped.
Figure 4.15. Results of stochastic model simulations of the B cap polymerization; uncapped fraction as a function of average cap length and the relative rate constants.

To ensure complete capping of every chain, enough butadiene monomer was transferred into the reactor to cap each chain with approximately 10–20 units. The polymerization of the cap was conducted at room temperature for 1.5 h, which is not enough time to consume all of the butadiene. The average number of B units per arm was estimated using $^1$H NMR and GPC analysis:

$$\langle B / \text{chain} \rangle = \left( \frac{x_{\text{cap}}^{n,r}}{x_{1^{st}\text{block}}^{n,r}} \right) \left( \frac{M_{n,r}}{M_0} \right) x_{1^{st}\text{block}}^{n,r}$$

[4.11]

where $x_i$ is the mole fraction of component $i$, $M_0$ is the mer molecular weight, and the 1$^{st}$ block is either B or S, depending on the polymer. For polymers containing a B block in addition to the cap, $x_{\text{cap}}$ is given by equation [4.12].
\[ x_{\text{cap}} = \frac{x_{B,\text{capped}} - x_{B,\text{uncapped}}}{1 - x_{B,\text{uncapped}}} \quad [4.12] \]

The first term in equation [4.11] is the number of B units in the cap per mer in the 1st block, and the second term is the number of 1st block units per chain. The results are shown in Table 4.6; based on the results of the stochastic simulations the experimental values of \(<B/\text{chain}>\) are sufficient to ensure that each chain has a minimum of 2 B units.

**Table 4.6. B Cap Lengths for Star TPEs**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(&lt;B/\text{chain}&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C-EP(_E))_6</td>
<td>8.9</td>
</tr>
<tr>
<td>(E-EP(_E))_6</td>
<td>6.8</td>
</tr>
<tr>
<td>(E-C-EP(_E))_6</td>
<td>7.3</td>
</tr>
</tbody>
</table>
4.4. Conclusions

In conclusion, block copolymers comprising linear low density polyethylene, polyvinylcyclohexane, and poly(ethylene-alt-propylene) were designed using a pseudo-diblock approach which made use of experimental measurements of the segmental interaction parameters ($\chi$) and the theoretical phase portrait. Linear and star block copolymer TPEs were synthesized by sequential anionic polymerization of butadiene, styrene, and isoprene followed by chlorosilane coupling and catalytic hydrogenation. Butadiene blocks were synthesized in neat cyclohexane to minimize 1,2-addition; the resulting saturated blocks had 20 ethyl branches/1000 C. Benzene (1:1 v/v to cyclohexane) was subsequently added to improve the rate of crossover to styrene. The coupling reaction was facilitated by the accelerating agent tetrahydrofuran, which enabled rapid, highly efficient coupling with a difunctional or hexafunctional chlorosilane terminating agent. To reduce degradation of the 6-arm stars during hydrogenation a short run of butadiene units was added to the block copolymer arms prior to coupling. The concomitant reduction in steric strain at the core was found to nearly eliminate arm loss during hydrogenation.
4.5 References


60. Daoulas, K. C.; Theodorou, D. N.; Roos, A.; Creton, C. Macromolecules 2004, 37, 5093-5109.


Chapter 5

Linear Block Copolymer Thermoplastic Elastomers with Composite Crystalline-Glassy Hard Domains

Having discussed the preparation of block copolymers with crystalline (polyethylene, E), glassy (polyvinylcyclohexane, C), and rubbery (poly(ethylene-alt-propylene, EP) blocks, this chapter discusses their use as thermoplastic elastomers (TPEs). Throughout the chapter two linear pentablock copolymers with composite crystalline-glassy “hard” blocks, (E-C-EP)$_2$-1 and (E-C-EP)$_2$-2, are compared with triblock copolymers with crystalline or glassy hard blocks, (E-EP)$_2$ and (C-EP)$_2$, respectively. Details of the molecular characterization are given in Chapter 4. The pentablocks differ in the ratio of the crystalline to glassy block fractions, given as the trailing number (-1 or -2). The phase behavior is first addressed through a combination of small-angle x-ray scattering, atomic force microscopy, and differential scanning calorimetry. The implications of the phase behavior for the processability of the TPEs are assessed using steady-shear and small-amplitude oscillatory shear rheology. The mechanical performance—including the Young’s modulus, ultimate properties, and recovery—is characterized by tensile testing and dynamic mechanical thermal analysis. Finally, these materials are compared with other semicrystalline TPEs in an attempt to elucidate the important design parameters.
5.1 Phase Behavior and Solid-State Structure

The temperature-dependent phase behavior of each polymer was assessed by small-angle x-ray scattering (SAXS) and differential scanning calorimetry (DSC); the results are summarized in Table 5.1. The discussion begins with the all-amorphous (C-EP)$_2$, which serves as a stand-in for commercial triblock copolymer TPEs. Figure 5.1 shows the SAXS patterns for (C-EP)$_2$ at room temperature and at 200 °C. The room temperature pattern initially showed only a single broad scattering maximum at $q^* = 0.152$ nm$^{-1}$ ($d = 2\pi/q^* = 41$ nm, pattern not shown), indicating that the material was microphase-separated, but that the long-range order was poor. The long-range order was improved slightly by heating to 200 °C and cooling back down to room temperature. The primary peak became sharper and more intense ($q^* = 0.169$ nm$^{-1}$, $d = 37$ nm), but clear higher-order peaks were not observed, save for the emergence of a shoulder near $q \approx 0.3$ nm$^{-1}$ (indicated by an arrow in Figure 5.1). These patterns precluded an unambiguous assignment of the morphology, which is not uncommon for highly compositionally asymmetric block copolymers which often become kinetically trapped in non-equilibrium morphologies due to their slow ordering kinetics. Nonetheless, the sharp primary peak persists at 200 °C almost unchanged ($q^* = 0.167$ nm$^{-1}$, $d = 38$ nm), indicating that the melt remains ordered to at least 200 °C.
Table 5.1. Morphological and Thermal Characteristics of Linear Block Copolymer TPEs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>d (nm)</th>
<th>—Compression Molded—</th>
<th>—Cooled at 10 °C/min—</th>
<th>T_g,EP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-EP)_2</td>
<td>49</td>
<td>102</td>
<td>4.1</td>
<td>26.4</td>
</tr>
<tr>
<td>(E-C-EP)_2-2</td>
<td>60</td>
<td>100</td>
<td>3.8</td>
<td>14.1</td>
</tr>
<tr>
<td>(E-C-EP)_2-1</td>
<td>44</td>
<td>93</td>
<td>3.3</td>
<td>9.3</td>
</tr>
<tr>
<td>(C-EP)_2</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values marked with a superscript b are apparent values calculated using equation [3.10].

Values marked with a superscript a are crystal thickness estimated from $T_m$ using the Gibbs-Thomson equation for crystallites of large lateral extent (equation [2.1]) with parameters $T_m^0 = 141.9 \, ^\circ C$, $\Delta H_{m,100} = 277 \, J/g$, and $\sigma = 55 \, \text{erg/cm}^2$.

Figure 5.1. SAXS patterns of (C-EP)_2 at room temperature and 200 °C. The arrow marks the higher-order feature. The absolute intensity ($I/I_e V$) is multiplied by $q$ to approximately correct for the form factor of cylindrical C domains. The intensity at 200 °C has been multiplied by 2 for clarity.
Based on the composition ($\phi_C = 0.18$) and the estimated segregation strength ($\chi N \approx 60$ at 20 °C and 40 at 200 °C) of (C-EP)$_2$, the equilibrium morphology of this polymer falls near the phase boundary between body-centered cubic spheres (BCC) and hexagonally packed cylinders (HEX). The precise position of the BCC-HEX phase boundary is sensitive to the conformational asymmetry ($b_A/b_B$, where $b_i$ is the statistical segment length of block $i$). Literature values vary substantially; the internally consistent analysis of Fetters et al. gives $b_C/b_{EP} = 1.1$, but the values reported by Cochran et al. yield $b_C/b_{EP} = 0.67$, a qualitatively different result. Moreover, the solid-state morphology corresponds to the morphology at the C domain glass transition temperature ($T_g = 145$ °C), which becomes kinetically arrested when the C domains vitrify. It is clear that predicting the equilibrium morphology of (C-EP)$_2$ a priori is not trivial.

Although the lack of long-range order in (C-EP)$_2$ does not allow for a direct determination of the nanoscale structure by SAXS, some ancillary evidence can be used to deduce the morphology of the C domains. Form factor calculations for cylindrical or spherical C domains were compared against the SAXS patterns in an effort to distinguish between the two. The form factor for infinitely long cylinders ($P_{cyl}$) can be approximated by:

$$P_{cyl}(q) \approx \frac{1}{q} \left[ \frac{2J_1(qR_{cyl})}{qR_{cyl}} \right]^2$$

[5.1]

where $J_1$ is the Bessel function of the first kind. SAXS patterns for cylindrical morphologies are plotted as the absolute intensity ($I/I, V$) multiplied by $q$ to approximately correct for the factor of $1/q$ in $P_{cyl}$. The cylinder radius ($R_{cyl}$) can be approximated by assuming a hexagonal packing where ($d^* = d_{10}$):
\[ R_{\text{cyl}} \approx \frac{2\pi}{q^*} \left[ \frac{2}{\sqrt{3}\pi} \phi_c \right]^{1/2} \]  

[5.2]

The form factor for spherical domains \( (P_{\text{sph}}) \) can be written as:

\[ P_{\text{sph}}(q) = \left[ 3 \sin(q R_{\text{sph}}) - q R_{\text{sph}} \cos(q R_{\text{sph}}) \right] \left( q R_{\text{sph}} \right)^3 \]

[5.3]

where the sphere radius \( (R_{\text{sph}}) \) can be approximated by assuming the spheres are packed on a BCC lattice:

\[ R_{\text{sph}} \approx \frac{2\pi}{q^*} \left[ \frac{3\sqrt{2}}{4\pi} \phi_c \right]^{1/2} \]  

[5.4]

Form factor calculations for \((\text{C-EP})_2\) at room temperature and 200 °C are shown in Figures 5.2 and 5.3. The locations of the structure factor peaks for the HEX or BCC morphologies are also indicated by triangles. Since the scattered intensity is proportional to the product of the form factor and the structure factor, minima in \( P \) should correspond to minima in intensity. Comparing \( P_{\text{cyl}} \) and \( P_{\text{sph}} \) to the data, it is clear that the minimum in \( P_{\text{cyl}} \) corresponds to a local dip in intensity while for \( P_{\text{sph}} \) the first minimum overlaps with the shoulder near \( q \approx 0.3 \) nm\(^{-1}\). Additionally, the positions of the second and third order structure factor peaks of HEX (\( q/q^* = \sqrt{3}, \sqrt{4} \)) correspond well with the shoulder in the SAXS pattern, while the BCC structure factor does not correspond well with the features in the data. Therefore, though not ordered on a regular hexagonal lattice, the morphology of the C domains is tentatively assigned as cylindrical. This result is corroborated by polystyrene-polyisoprene (S-I) diblocks\(^5,9\) and S-I-S triblocks\(^10\) with similar compositions, which exhibit cylindrical S domains.
Figure 5.2. SAXS pattern of (C-EP)$_2$ at room temperature (solid) with $P_{cyl}$ (a) and $P_{sph}$ (b) form factor calculations (dashed). Structure factor peak positions are indicated by triangles for HEX: $q/q^* = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}$ and for BCC: $q/q^* = 1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}$. From equations [5.2] and [5.4] $R_{cyl} = 9.6 \text{ nm}$ and $R_{sph} = 14.7 \text{ nm}$.
Figure 5.3. SAXS pattern of (C-EP)₂ at 200 °C (solid) with $P_{cyl}$ (a) and $P_{sph}$ (b) form factor calculations (dashed). Structure factor peak positions are indicated by triangles for HEX: $q/q^* = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}$ and for BCC: $q/q^* = 1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}$. From equations [5.2] and [5.4] $R_{cyl} = 9.3$ nm and $R_{sph} = 14.9$ nm.
The real-space structure of (C-EP)\textsubscript{2} was imaged at room temperature using atomic force microscopy (AFM) on an annealed 120 nm thick film. Height and phase images (Figure 5.4) revealed a disordered collection of circular C domains, dispersed in a rubbery matrix. Image analysis yielded an average radius of 9.4 nm for the dispersed domains, in excellent agreement with $R_{\text{cyl}} = 9.6$ nm calculated using equation [5.2], further affirming the assignment of cylinders. Thus, the circular objects in the AFM image are evidently C cylinders viewed end-on.
Figure 5.4. AFM height (a) and phase (b) images of an annealed film of (C-EP)$_2$. 
The SAXS pattern of (E-EP)$_2$ at room temperature (Figure 5.5) reveals a weak first-order peak ($q^* = 0.128$ nm$^{-1}$, $d = 49$ nm) followed by a broad hump, indicating a heterogeneous structure with a broad distribution of length scales. The pattern reflects a pseudo-lamellar morphology which arises from the strong tendency of E to form lamellar crystals, despite the large compositional asymmetry.$^{11,12}$ The local parallel arrangement between crystallites can be seen in the AFM phase image shown in Figure 5.6. Though the AFM image agrees with the morphological picture of semicrystalline block copolymers crystallized from a homogeneous melt, the image shows featureless regions that far exceed the characteristic dimensions of the amorphous EP block. Hard domains in these regions are likely obscured by a wetting layer of the rubbery phase, or are undetectable due to unfavorable orientation. The matter of the inverted contrast in Figure 5.6, in comparison with the more conventional scenario where hard domains appear bright (cf. Figure 5.4b), will be addressed subsequently. When the material is heated above the melting point ($T_m = 101$ °C), the pattern abruptly becomes featureless. The electron density contrast between amorphous E$^{13}$ and EP$^{14}$ at 110 °C is too small ($\Delta \rho_e < 1$ e$^-$/nm$^3$) to detect microphase separation by SAXS, even if present. However, as noted in the preceding chapter, $\chi$ between E and EP is small; the estimated$^{15}$ segregation strength for this polymer is half of what is theoretically$^4$ required for microphase separation for an A-B-A triblock copolymer. Therefore, (E-EP)$_2$ is expected to be entirely homogeneous in the melt. For comparison, the estimated$^{15}$ $\chi N$ for (C-EP)$_2$ is nearly twice ($\chi N)_{ODT}$ even at 200 °C.
Figure 5.5. SAXS patterns of (E-EP)$_2$ at room temperature and 110 °C; the absolute intensity is multiplied by $q^2$ to approximately correct for the form factor of lamellae.

Figure 5.6. AFM phase image of (E-EP)$_2$. 
Having established the striking difference in phase behavior between triblocks with C and E end blocks, the SAXS patterns of the pentablock copolymers are now examined. Figure 5.7 shows the SAXS patterns for \((E-C-EP)_{2-2}\) at room temperature and just above \(T_m\). At room temperature the most intense feature is the primary peak at low \(q (q^* = 0.105 \text{ nm}^{-1}, d = 60 \text{ nm})\) followed by a broad hump centered near \(q = 0.6 \text{ nm}^{-1}\). The low-\(q\) feature arises from the average spacing between composite crystalline-glassy domains, while the broad hump carries information about the interior structure of these domains. Assuming this peak arises from the interlamellar spacing of the E crystallites, the crystal thickness \((t_c)\) was estimated by \(t_c = d\phi_{c,E}\), where \(d\) is calculated from the position of the broad hump in the SAXS pattern and \(\phi_{c,E}\) is the volume fraction of E which is crystalline (calculated using the weight fraction crystallinity \((w_{c,E})\) from DSC). The estimated \(t_c = 4.5 \text{ nm}\) is in good agreement with previous reports for hydrogenated polybutadienes of this ethyl branch content.\(^{11}\) Just above \(T_m\), at 110 °C, the SAXS pattern is featureless. If microphase separation were to occur it would be expected to arise between the C block and the other blocks. There is more than enough electron density contrast \((\Delta \rho_e > 40 \text{ e}^{-}/\text{nm}^3)\) to detect such a situation by SAXS; therefore, the featureless pattern definitively confirms that the melt is disordered.
Figure 5.7. SAXS patterns of (E-C-EP)$_2$-2 at room temperature and 110 °C; the absolute intensity is multiplied by $q^2$ to approximately correct for the form factor of lamellae.

AFM images of (E-C-EP)$_2$-2 are shown in Figure 5.8; two scans of the same region of the sample are shown. For this polymer, as with (E-EP)$_2$, the best images were obtained when the sample was minimally engaged by the AFM tip (shown in panels (a) and (b)); in this attractive regime the less dissipative (hard) domains appear dark.$^{16}$ Engaging the sample more strongly (by reducing the amplitude set point) restores the more familiar phase contrast where higher-modulus regions appear bright in the phase image (Figure 5.8d). While this improves the resolution of the height images (cf. Figures 5.8a and 5.8c), the quality of the phase images is markedly reduced (cf. Figures 5.8b and 5.8d). Regardless of the imaging regime, the phase image in panel (b) and the height image in panel (c) both show string-like arrangements of composite hard domains. The distance between nodules both along a string and between
adjacent strings is consistent with the ≈60 nm long spacing from SAXS, confirming that the primary peak reflects the average spacing between composite hard domains. This structure arises from growing E crystallites which are “pinched off” by the formation of C domains (dark nodules in the image) as they attempt to form the preferred lamellar structure. AFM images of pentablock copolymer TPEs investigated by Bishop and Register showed evidence of similar structures.17
Figure 5.8. AFM height (a) and phase (b) images of (E-C-EP)_2-2 displaying inverted phase contrast compared to height (c) and phase images (d) of the same region with conventional phase contrast.
(E-C-EP)$_2$-1 exhibits the same limiting phase behavior—a structured solid below $T_m$ and a homogeneous melt above $T_m$—with some added complexity in the melt (Figure 5.9). Below $T_m$, the solid-state SAXS pattern shows a low-$q$ primary peak ($q^* = 0.142$ nm$^{-1}$, $d^* = 44$ nm) followed by a broad tail extending to $q \approx 1$ nm$^{-1}$ with no discernible maximum. The AFM phase image in Figure 5.10 shows ramified structures which coexist with small discrete hard domains (bright spots in the upper right corner) highlighting the complexity of structure formation by combined crystallization and vitrification. Just above $T_m$, the primary SAXS peak and broad tail give way to a single broad peak at intermediate $q$ ($q = 0.263$ nm$^{-1}$, $d = 24$ nm). The breadth and temperature dependence of this peak are consistent with correlation hole scattering, indicating that the melt is disordered but in close proximity to the phase boundary at 110 °C.$^{18,19}$ This is not surprising given that this polymer was designed to have a disordered melt with the highest possible segregation strength (see Chapter 4).

Using the same block chemistries, Bates and coworkers observed similar behavior in block copolymers with the general architecture X-EP-X where X is either C-E-C-E-C$^{20}$ or C-E-C.$^{15,21}$ Interestingly, in the polymers studied by Bates et al. the position of the correlation hole peak corresponds to $q^*$ in the solid state. The authors attribute this to crystal nucleation within E-rich regions followed immediately by vitrification of the C-rich regions, locking in the length scale associated with the compositional inhomogeneities associated with the correlation hole scattering. In the case of (E-C-EP)$_2$-1 the position of the solid-state and correlation hole peaks in the SAXS patterns differ widely, indicating that crystallization of the E blocks is not confined to the length scale associated with the correlation hole.
Figure 5.9. Temperature dependent SAXS patterns of (E-C-EP)$_2$-1; the absolute intensity is multiplied by $q^2$ to approximately correct for the form factor of lamellae.

Figure 5.10. AFM phase image of (E-C-EP)$_2$-1.
Differential scanning calorimetry (DSC) offers some additional insight into the phase behavior and structure of these materials. Figure 5.11 shows DSC traces of the four TPEs on cooling and heating. DSC traces on dynamic cooling from the melt (Figure 5.11a) show bimodal crystallization peaks for both pentablocks compared to the sharp, monomodal peak of (E-EP)$_2$. This feature is interpreted as a two-stage crystallization process illustrated in Figure 5.12. Crystallization initially proceeds from a homogeneous melt. However, due to the connectivity of the blocks, crystallization of the E blocks concentrates the adjacent C segments in the vicinity of the crystallites thereby imparting a degree of segregation between the C and EP blocks, which would otherwise be miscible. The crystallization-induced aggregation of the C blocks, in turn, restricts the mobility of the E segments, retarding crystal growth. The characteristic length scale separating these composite hard domains is on the order of 50 nm, as determined from the primary peaks in the SAXS patterns. As the undercooling is increased further, crystallization resumes within the now isolated composite E-C domains. In (E-C-EP)$_2$-2 the two crystallization peaks are heavily overlapped (peak-to-peak separation of only 4 °C) indicating that the short C blocks provide minimal interference. On the other hand, (E-C-EP)$_2$-1 shows two clearly resolved peaks separated by some 24 °C. The large additional undercooling required to fully crystallize (E-C-EP)$_2$-1 is ascribed to the proximity to the order-disorder transition, which enhances the segregation between C and EP, producing higher-purity C domains.
Figure 5.11. Differential scanning calorimetry traces of the three semicrystalline polymers on cooling (a) and all four linear polymers on heating (b) at 10 °C/min.
**Figure 5.12.** Illustration of the phase behavior of the pentablock TPEs. Blue blocks represent E, C is represented by bold green blocks for emphasis, and EP is red. The top panel depicts the homogeneous melt above $T_m$; in the center, below the crystallization temperature ($T_c$), crystallization begins to establish physical cross-links but is hindered by aggregation of the adjacent C blocks; on the bottom, C blocks vitrify and E blocks continue to crystallize upon further cooling.
The impact of the C blocks on crystallization can also be inferred from the melting point and degree of crystallinity of the E blocks ($w_{c,E}$) (Table 5.1). The crystal melting point depends sensitively on crystallite size, in particular the thickness.\textsuperscript{23,24} In the absence of other constraints, the melting point ($T_m \approx 100-105 \, ^\circ C$) and crystallinity ($w_{c,E} \approx 0.4$) of the E blocks is fundamentally limited by the randomly distributed ethyl branches arising from 1,2-addition in the precursor polybutadiene.\textsuperscript{23-26} (E-C-EP)$_2$-2 has a melting point 2 \, ^\circ C below that of (E-EP)$_2$, revealing a reduction in the size of the crystallites. A more significant change in crystallite size is inferred from the peak melting temperature of (E-C-EP)$_2$-1, which is 10 \, ^\circ C lower than that of (E-EP)$_2$. It is likely that the presence of the C blocks reduces both the lateral dimensions and the thickness of the crystal; however, the melting point is far more sensitive to changes in the crystal thickness. Using the Gibbs-Thomson equation\textsuperscript{2,27} for E crystals of large lateral extent one calculates a decrease in crystal thickness of 0.2 nm for (E-C-EP)$_2$-2 and 0.8 nm for (E-C-EP)$_2$-1 compared to (E-EP)$_2$.

Using the same architecture and block fractions with different block chemistries, Bishop and Register\textsuperscript{17} observed a dramatic reduction in $w_c$ of the crystalline end blocks when the glassy block fraction was increased (from $w_c = 0.54$ to 0.15 when the glassy block fraction was doubled at constant total hard block fraction). Interestingly, in the present case the melting enthalpy ($\Delta H_m$) measured by DSC apparently scales non-monotonically with glassy block content (Table 5.1). (E-C-EP)$_2$-2 has the highest apparent $\Delta H_m$, which may reflect an extra enthalpic contribution from an underlying C glass transition rather than an actual increase in $w_{c,E}$. Similarly, a reduction in $w_{c,E}$ in (E-C-EP)$_2$-1 may be masked by an underlying contribution of the C blocks. It should be noted that the measured $T_g$ of the C domains cannot exceed $T_m$, since the C domains dissolve into the disordered state when the crystals melt. Thus, if the true $T_g$ is near
or even above $T_m$ the enthalpic contribution of the glass transition necessarily overlaps with the melting endotherm. Although the $T_g$ of the C domains cannot be observed directly, all four polymers exhibit a $T_g$ near $-60 \, ^\circ\text{C}$, in good agreement with the $T_g$ of EP homopolymer\textsuperscript{15,28}, indicating substantial segregation between the C and EP blocks. The crystallinity of all three semicrystalline TPEs is sufficient to render them insoluble to at least 50 °C in cyclohexane, toluene, and tetrahydrofuran, good solvents for all three constituent blocks above $T_m$. Since $T_m$ and $w_{c,E}$ are inherently limited by short-chain branching, both were found to be largely insensitive to thermal history.

### 5.2 Melt Rheology

The connection between the phase behavior and melt processability was explored using steady-shear and small-amplitude oscillatory shear (SAOS) rheometry at 180 °C. Figure 5.13 shows viscosity curves for each of the linear polymers constructed from the steady-shear ($\eta$) and the complex viscosity ($\eta^*$, from SAOS) using the Cox-Merz rule.\textsuperscript{29} The pentablocks and (E-EP)$_2$, all of which exhibit homogeneous melts at 180 °C, show viscosities in the range of $1–3\times10^4$ Pa\textperiodcentered s with clear zero-shear-rate plateaus. The incremental increases in viscosity from (E-EP)$_2$ to (E-C-EP)$_2$-2 to (E-C-EP)$_2$-1 reflect the increase in C content. On the other hand, at low shear rates the viscosity of (C-EP)$_2$ is more than two orders of magnitude larger and shear thinning is observed even at the lowest shear rates tested; both features are consequences of the microphase-separated melt structure.
Figure 5.13. Viscosity curves for the block copolymer TPEs; filled symbols indicate steady-shear viscosity ($\eta$) plotted against the shear rate ($\dot{\gamma}$) and open symbols correspond to complex viscosity ($\eta^*$) plotted against angular frequency ($\omega$).

When probed by SAOS (Figure 5.14), all three E-containing polymers exhibit terminal behavior (elastic modulus $G' \sim \omega^2$ and loss modulus $G'' \sim \omega^1$ at low $\omega$) indicating that the melts behave as simple polymeric liquids, as anticipated from the SAXS results. On the other hand, (C-EP)$_2$ does not display terminal behavior, but instead retains substantial elastic character even at the lowest frequencies tested. At high frequencies all four polymers exhibit the same limiting $\eta^*$ and $G'$ meaning that when the rate of deformation is sufficiently high the processability is similar. The full range of deformation rates is relevant during processing (e.g., injection molding), and the marked difference in the behavior at low rates is particularly important for molding fine features.
Figure 5.14. Small-amplitude oscillatory shear storage modulus, $G'$, (a) and loss modulus, $G''$, (b) versus frequency. Terminal scaling is shown by the solid lines.
5.3 Mechanical Properties

With the phase behavior and structure of the four polymers established, their performance as elastomers was assessed in uniaxial extension. Figure 5.15 shows representative stress-strain curves for each of the four polymers; all four polymers display elastomeric behavior characterized by low Young’s modulus ($E_Y$), strain hardening, and high extensibility (large breaking strain). The ultimate stress ($\sigma_u$), strain ($\varepsilon_b$), and toughness ($T_u$), and $E_Y$ were measured from a minimum of three specimens (Table 5.2). To facilitate comparison with TPEs with rubbery blocks other than EP the Young’s modulus is also presented in terms of the modulus ratio $E_Y/E_N^0$, where $E_N^0$ is the plateau modulus of the uncross-linked rubbery component, for EP $E_N^0 = 3.45$ MPa.\(^{30}\) The intrinsic ultimate properties are difficult to measure experimentally due to premature failure induced by impurities or imperfections in the test specimen, so the maximum measured $\sigma_u$ and the corresponding $\varepsilon_b$ are also reported.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_Y$(^a) (MPa)</th>
<th>SD(^b) (%)</th>
<th>$E_Y/E_N^0$</th>
<th>$\sigma_u$(^c) (MPa)</th>
<th>SD(^b) (%)</th>
<th>$\varepsilon_b$(^c) (%)</th>
<th>SD(^b) (%)</th>
<th>$T_u$ (MJ/m(^3))</th>
<th>SD(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-EP)(_2)</td>
<td>10.2</td>
<td>2</td>
<td>2.9</td>
<td>6.4 / 6.4(^a)</td>
<td>1</td>
<td>19.0 / 19(^a)</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(E-C-EP)(_2)-2</td>
<td>8.4</td>
<td>3</td>
<td>2.4</td>
<td>7.7 / 7.5</td>
<td>2</td>
<td>51.5 / 46</td>
<td>11</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(E-C-EP)(_2)-1</td>
<td>6.7</td>
<td>4</td>
<td>1.9</td>
<td>8.4 / 6.9</td>
<td>20</td>
<td>29.1 / 22</td>
<td>31</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(C-EP)(_2)</td>
<td>7.1</td>
<td>34</td>
<td>2.1</td>
<td>11.0 / 9.6</td>
<td>21</td>
<td>34.1 / 29</td>
<td>22</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Average and \(^b\)one standard deviation of at least 3 specimens, \(^c\)maximum measured value; for (C-EP)\(_2\) the maximum $\sigma_u$, $\varepsilon_b$, and $T_u$ were measured in three different specimens; for all other polymers the maximum values were measured in a single specimen.
Figure 5.15. Uniaxial stress-strain curves for each of the four linear TPEs.

In the case of (C-EP)$_2$, microphase separation yields well-dispersed C domains leading to a modest increase in modulus (Table 5.2). The large variability in the modulus of (C-EP)$_2$ is consistent with cylindrical C microdomains, where the stress-strain behavior is sensitive to the orientation of the cylinders with respect to the stretching direction.\textsuperscript{10,31,32} The compression-molded films used for tensile tests were strongly birefringent when viewed through crossed polarizers, indicative of preferential orientation,\textsuperscript{33} a well-documented occurrence when strongly-segregated melts with anisotropic domains are subjected to flow.\textsuperscript{32,34} Of the six specimens tested, one had a modulus of 11.8 MPa, nearly twice the average of the other five (6.0 ± 0.8 MPa). The high modulus and prominent yield point near 15% strain observed in this specimen are consistent with a cylindrical morphology where the cylinder axes are principally coincident with the stretching direction.\textsuperscript{10,31,32} Excluding this sample due to its apparent alignment (corroborated by a Q test with 95% confidence), the remaining five samples show the lowest
modulus ratios \( (E_Y/E_N^0 = 1.7 \pm 0.2) \) of the four TPEs. Though this modulus ratio is generally consistent with model\(^{35}\) predictions for \( E_Y/E_N^0 = 1.5–1.9 \) for a rubber filled with isotropic hard spheres (with filler fraction \( \phi_C = 0.18 \)), the large sample-to-sample variability is consistent with cylindrical C domains.

Using a single S-I-S triblock (18.3 wt% S) Orimo and Hotta\(^{36}\) showed that the Young’s modulus of a specimen with a BCC morphology was 10% higher than that of a specimen with a disorganized spherical phase. Thus, the observed factor-of-two discrepancy in \( E_Y \) observed in specimens of (C-EP)\(_2\) cannot be explained by fortuitous ordering of spherical domains onto a BCC lattice. Using the same polymer Orimo and Hotta found that the Young’s modulus of the unoriented hexagonally-packed cylindrical morphology was 70% larger than that of the disorganized sphere-forming phase. Although the morphology and orientation of (C-EP)\(_2\) likely depend on the processing history, four of the six specimens (including the specimen with \( E_Y = 11.8 \) MPa) were cut from a single molded film, so large specimen-to-specimen variations in the morphology (i.e. spherical versus cylindrical) are unlikely. In macroscopically-oriented, cylinder-forming S-I-S triblocks \( E_Y \) measured in the direction coincident with the cylinder axes can be as much as an order of magnitude larger than \( E_Y \) in the perpendicular direction.\(^{37}\) Thus, the high modulus and prominent yielding observed in a few specimens of (C-EP)\(_2\) are characteristic of a cylindrical morphology in which the long axes are primarily aligned with the stretching direction.

At the other extreme, the crystallization-driven lamellar morphology of (E-EP)\(_2\) is responsible for the larger modulus ratio \( (E_Y/E_N^0 = 2.9) \), which is undesirable for a soft elastomer. It should be noted that this effect is mitigated by the moderate degree of crystallinity of the E blocks (Table 5.1); although (E-EP)\(_2\) has the same end block weight fraction as (C-EP)\(_2\), the
effective hard domain content is approximately half. Similar polymers with higher crystallinity end blocks exhibit modulus ratios of 10 or more.\textsuperscript{17,38} The plate-like morphology and interconnectivity of the crystallites are responsible for the modulus increase. The ultimate strength of (E-EP)\textsubscript{2} is also significantly less than that of (C-EP)\textsubscript{2}. This is attributed to the comparatively poor strength of the crystallites, which are prone to a variety of yielding mechanisms.

Incorporating C blocks into the pentablock architecture simultaneously reduced $E_Y$ and increased the maximum observed $\sigma_u$ (Table 5.2, Figure 5.16), both of which are desirable effects. It can be seen in Figure 5.16 that (E-C-EP)\textsubscript{2}-1 outperforms (E-C-EP)\textsubscript{2}-2 in both of these metrics, illustrating that a higher glassy block content can provide greater improvement. The reduction in modulus is attributed to the effect of the C on the continuity of the hard domains. In the pentablock copolymers aggregation of the C blocks near the growing crystallites limits lateral growth (as illustrated in Figure 5.12) and preventing highly interconnected higher-order structures (i.e., spherulites) from forming. A similar argument can be made for the effect of the C content on $\sigma_u$; the vitreous C layer surrounding the E crystallites evidently bears some portion of the stress and inhibits failure by processes like chain pullout and crystal fragmentation. The high-strain yield point in (E-C-EP)\textsubscript{2}-2 was observed in all three samples tested and resembles the stress-strain curve of E-EP-E triblock copolymers reported previously.\textsuperscript{39-41} This feature will be discussed in further detail subsequently. Although the E end blocks alone provide qualitatively elastomeric mechanical characteristics (owing to their modest crystallinity), it is impossible to simultaneously reduce $E_Y$ and increase $\sigma_u$ simply by changing the E block content.\textsuperscript{40-44} A triblock copolymer with 10 wt\% E was prepared and tested to illustrate this point; $E_Y$ for this
polymer was reduced \( (E_y/E_N^0 = 1.71 \pm 0.06) \), but the ultimate properties were dramatically diminished \( (\sigma_u = 1.39 \pm 0.01 \text{ MPa and } \varepsilon_b = 160 \pm 10\%) \).

![Graph showing Young's modulus and ultimate stress vs. C block weight fraction](image)

**Figure 5.16.** Young’s modulus and the maximum observed ultimate stress and toughness for the four linear TPEs plotted versus C block weight fraction.

The energy per unit volume required to break the specimen, or toughness \( (T_u) \) also increased as a function of the C block weight fraction (Figure 5.16). The increase in \( T_u \) is non-monotonic because the high-strain yielding observed in \( (E-C\text{-EP})_2-2 \) results in a comparatively large value of \( T_u \). Nonetheless, the highest measured toughness of the remaining three TPEs increases with increasing C block content. The improvement results from increases in \( \sigma_u \) and \( \varepsilon_b \), which more than compensate for fact that \( (E\text{-EP})_2 \) exhibits the highest stress at any given strain (Figure 5.15), i.e., \( (E\text{-EP})_2 \) is the stiffest of the four polymers.
The temperature dependence of the modulus is of particular importance for TPEs because the point at which the physical cross-links soften determines the upper use temperature of the material. Dynamic mechanical thermal analysis (DMTA) was used to probe the temperature dependence of the small-strain modulus in the four linear TPEs (Figure 5.17). Similar to the SAOS measurements, DMTA measures both the storage ($E'$) and loss components of the small-strain tensile modulus ($E''$) using an oscillatory strain profile. In the rubbery plateau region ($-40 \leq T \leq 60 \, ^\circ\text{C}$) the storage component dominates and $E'$ is comparable to $E_Y$. The ratio $E''/E' = \tan \delta$ is a measure of viscous dissipation; peaks in $\tan \delta$ indicate thermal transitions.
Figure 5.17. DMTA of TPEs: storage modulus, $E'$, (a), loss modulus, $E''$, (b), and tan δ (c).

Insets provide an expanded view of the rubbery region.
The upper use temperatures of the semicrystalline TPEs (≈60 °C) are significantly lower than that of (C-EP)$_2$ (>100 °C), primarily because the $T_m$ of E is some 40 °C below the $T_g$ of C. As with the DSC measurements, the $T_g$ of the C domains in the pentablocks was not directly observable by DMTA. The moduli of the E-containing polymers also show a stronger temperature dependence than in (C-EP)$_2$, due, in part, to thermally activated screw dislocations in the E crystallites (commonly referred to as the $\alpha$-relaxation).$^{45,46}$ (E-EP)$_2$ shows peaks in $E''$ and tan $\delta$ near 45 °C, consistent with the position ($T_\alpha$) of the $\alpha$-transition measured in a hydrogenated polybutadiene with similar branch content.$^{45}$ In the pentablocks, both the intensity and location of the $\alpha$-relaxation peak decrease with increasing C content. The former observation is attributed to the reduced overall degree of crystallinity due to the reduction in E content (regardless of whether the apparent $\Delta H_m$ values in Table 5.1 reflect the actual degree of crystallinity of the E blocks). The shift in $T_\alpha$ to lower temperatures is a result of the reduction in crystal thickness inferred from the $T_m$ measured by DSC (Table 5.1).$^{45,46}$ Though the $\alpha$-transition originates in the crystallites, its mechanical signature (peak in tan $\delta$ and reduction in $E'$) arises from the attendant relaxation in the rubbery phase. This leads to the conclusion that the regions near the crystal fold surfaces, which are enriched in C, are not completely vitreous due to segmental mixing with the rubbery E and EP segments.

In spite of the reduction in $T_\alpha$, all three semicrystalline TPEs perform well at elevated temperatures relative to similar semicrystalline TPEs. When heated from 25 °C to 50 °C, (E-EP)$_2$ and (E-C-EP)$_2$-2 show a 25% reduction in $E'$, while (E-C-EP)$_2$-1 exhibits only a 16% reduction; in all three polymers $E'$ drops by 50% when heated to 75 °C. These results can be compared to the available data on polyolefin block copolymers (OBCs) which comprise alternating blocks of linear low density polyethylene (similar to hydrogenated polybutadiene)
and a rubbery α-olefin/ethylene copolymer. The softest OBC studied by Wang et al.\textsuperscript{47} (OBC H18, $E' = 12$ MPa at 25 °C) softens by 50% at 50 °C and 70% at 75 °C. Stiffer OBCs ($E' = 36$–520 MPa) fare better, but still soften by 30% at 50 °C and 60% at 75 °C.

Another key characteristic of the mechanical behavior of TPEs is the ability to recover applied strain. To test the recovery, samples were serially strained and relaxed, increasing the applied strain ($\varepsilon_a$) in each successive cycle. The cumulative residual strain (set, $\varepsilon_s$) was measured at two time points for each cycle: the “initial” set is measured during the return cycle, and the “final” set was measured after the specimen was allowed to rest for 5 min. The results, cast in terms of the initial and final recovery ($R^i$ and $R^f$, respectively), are shown in Figure 5.18. All four polymers exhibited elastomeric behavior ($R \geq 90\%$) over the range of $\varepsilon_a$ tested, but the recovery of (C-EP)$_2$ was systematically higher than the three semicrystalline TPEs both initially and after the 5 min rest. The comparatively poorer performance of the materials with E end blocks is attributed to yielding and fragmentation of the crystallites. At low strains ($\varepsilon_a < 100\%$), where the reorientation of hard domains\textsuperscript{33,39} causes the recovery to be relatively poor after the first cycle, $R^i$ is slightly higher for pentablocks than (E-EP)$_2$. However, for $\varepsilon_a = 150$–500% (E-EP)$_2$ actually outperforms the two pentablocks in terms of $R^i$. After allowing the specimens to rest, $R^f$ is essentially indistinguishable for the three semicrystalline polymers. This indicates that the pentablocks recover more slowly than (E-EP)$_2$, but that the final permanent set is not strongly impacted by the presence of the glassy blocks.
Figure 5.18. Initial (a) and final (b) strain recovery of the four linear TPEs as a function of applied strain. Data points represent an average of three measurements and error bars represent one standard deviation.
Each specimen of (E-C-EP)$_2$-2 tested exhibited a yield point ($\varepsilon_y$) near 800% strain as seen in Figure 5.15. After failure ($\varepsilon_a = \varepsilon_b \approx 1000\%$), an estimated 90% of the deformation was recovered. Assuming that 95% of the deformation below $\varepsilon_y$ is recovered (Figure 5.18) indicates that only 70% of the post-yield deformation is recovered. The location of this feature distinguishes it from the well-studied yielding mechanisms of polyethylene homopolymers, which occur at much lower strains.\textsuperscript{48} As mentioned above, similar behavior was observed in E-EP-E triblocks studied by Mohajer et al.\textsuperscript{40,41} and Séguéla and Prud’homm.\textsuperscript{39} Using detailed structural characterization during deformation, Séguéla and Prud’homm attributed this feature to an irreversible fibrillar transformation of the E crystallites.\textsuperscript{49} A triblock copolymer with linear polyethylene end blocks, studied by Myers and Register,\textsuperscript{38} also exhibited a yield point distinct from that of polyethylene homopolymers ($\varepsilon_y \approx 370\%$). Thus the high-strain yield point appears to stem from irreversible deformation of the E blocks.

In addition to the recovery, another quantitative metric for elasticity is the fractional hysteresis ($H$). As the name implies, $H$ measures the difference between the loading and unloading curves in the cyclic strain test. Physically, $H$ measures the amount of energy dissipated as heat during deformation, which cannot be recovered on unloading. Thus, while a viscoelastic material will always show some dissipation, more elastic materials will show less hysteresis. Figure 5.19 shows $H$ plotted versus $\varepsilon_a$. Unlike the recovery, (C-EP)$_2$ exhibits larger $H$ on average than the semicrystalline TPEs, though the error bars for (C-EP)$_2$ include the other TPEs in many cases. The large variability in $H$ is again attributed to differences in the cylinder orientation with respect to the loading directions, which is corroborated by $E_Y$ measured on the first cycle. The best performing specimen of (C-EP)$_2$ had $H = 0.17$ on average, which is quite
competitive with the other polymers. Interestingly, the apparent cylinder orientation did not have a strong impact on the recovery.

![Figure 5.19](image.png)

**Figure 5.19.** Hysteresis as a function of applied strain for the four linear TPEs.

The three semicrystalline polymers show similar $H$ across the range of $\varepsilon_a$. The results for (E-EP)$_2$ are in excellent agreement with the findings of Mohajer et al. who studied a series of E-EP-E triblock copolymers prepared by sequential anionic polymerization and hydrogenation.$^{41}$ A triblock with 18 wt% E showed markedly similar hysteresis values (the initial strain rate was 0.017 s$^{-1}$ versus 0.036 s$^{-1}$ in this work); a plot of $H$ versus $\varepsilon_a$ was convex with a local minimum near $\varepsilon_a = 300\%$. The pentablocks are very similar to (E-EP)$_2$ in terms of $H$, though they do perform better below $\varepsilon_a = 100\%$, consistent with the recovery findings. The small-strain improvements in $R$ and $H$ of the pentablocks are again attributed to the limited lateral extent and reduced continuity$^{41}$ of the composite E-C domains. Though the performance of the pentablocks
is dominated by the crystalline blocks and is on par with \((E-EP)_2\) above \(\varepsilon_d = 100\%\), the thinner crystals in the pentablocks, particularly \((E-C-EP)_2\)-1, are expected to be more prone to yielding.\(^{50}\) The presence of the glassy blocks evidently offsets this effect.

### 5.4 Design Parameters for Semicrystalline Thermoplastic Elastomers

This section compares the TPEs presented in the preceding pages with other TPEs containing semicrystalline blocks reported in the open literature. In particular, the pentablock copolymers \((E-C-EP)_2\)-2 and \((E-C-EP)_2\)-1 are compared with other TPEs containing both crystalline and glassy blocks. The goal is to understand which of the many parameters are most important for designing high-performance TPEs with a semicrystalline component.

Though crystallization from the microphase-separated melt negates one of the primary advantages of using semicrystalline blocks, it is nonetheless important to understand the mechanical performance of such systems. Coates and coworkers demonstrated elastomeric properties using triblock copolymers with high-crystallinity polypropylene end blocks.\(^ {51,52}\) The modest modulus ratios \(\left(\frac{E_Y}{E_N^0} \approx 2\right)\)\(^ {30}\) can be attributed to the fact that crystallization of the end blocks is confined by the microphase-separated structure in the melt. Though the recovery was reasonably high, substantial plastic deformation of the crystallites led to large hysteresis. Kong et al.\(^ {53}\) studied triblock copolymers with semicrystalline poly(\(L\)-lactide) (PLLA) end blocks, which showed evidence of microphase-separated melts. By examining a range of block molecular weights, the authors concluded that higher crystallinity is detrimental to the elastomeric properties. Wanamaker and coworkers\(^ {54}\) have reported similar TPEs with semicrystalline PLLA or poly(\(D\)-lactide) (PDLA) end blocks, which are microphase-separated with poor long-range order above \(T_m\). Interestingly, they found that \(E_Y\) for blends of triblocks
with PLLA and PDLA end blocks, which form a stereocomplex, was higher than $E_Y$ for either of the neat triblocks. In some cases the modulus was increased by more than a factor of 3.5 while the degree of crystallinity was essentially unaffected. This phenomenon might be ascribed to changes in the morphology of the crystals upon stereocomplexation. Based on these results, it appears that both crystallinity and crystal morphology are important for determining the mechanical properties.

The importance of these two parameters is most clearly seen by comparing triblock polymers with polyethylene end blocks derived from different sources. Polyethylene blocks derived from hydrogenated polybutadiene (E), such as those described here, have been studied extensively. In these systems qualitatively elastomeric behavior—relatively low modulus ratios, strain hardening, and good recovery—can be achieved with the appropriate block fractions. Increasing the E block fraction gradually imparts more plastic character to the mechanical response; however, even at 50% E the modulus is modest ($E_Y/E_N = 5.1$) and the shape of the stress-strain curve resembles that of a TPE. In contrast, truly linear polyethylene (LPE) end blocks—which are free of short chain branches, leading to larger (both in terms of thickness and lateral dimensions), more interconnected crystals and higher degrees of crystallinity—show qualitatively different behavior. An LPE-hPHN-LPE triblock (where hPHN is rubbery hydrogenated polyhexynorbornene) with 20 wt% LPE exhibited a larger modulus ratio ($E_Y/E_N = 9.1$) and a prominent yield point near 370% strain. Prior to yielding, the triblock exhibited strain hardening and good recovery, consistent with TPE behavior, but the post-yield deformation is likely largely unrecoverable. Espinosa et al. investigated an LPE-polyisobutylene-LPE triblock with 40 wt% LPE found $E_Y/E_N > 100$, characteristic of a plastic rather than an elastomer.
The influence of crystallinity and crystal morphology on the mechanical properties is borne out by comparing \((E-EP)_2\), and polymers like it, with LPE-hPHN-LPE. At a constant hard block content (20 wt%) the difference between E and LPE is clear, and might be falsely ascribed to the difference in crystallinity \(w_{c,E} = 0.48\) versus \(w_{c,LPE} = 0.64\). However, when LPE-hPHN-LPE is compared to E-EP-E triblock copolymers\(^{12,41}\) with comparable overall crystallinity \(w_c = w_{c,E} \times w_E \approx 15\%\) it becomes clear that the degree of crystallinity is not the controlling parameter.

The E-EP-E polymers have lower moduli \(E_Y/E_N^0 = 5.1\) versus \(9.1\) and retain elastomeric character to higher strains. This qualitative difference in performance is attributed to the difference in the morphology of the crystallites. Inherently low-crystallinity end blocks, such as E, produce crystallites of limited size and connectivity, which in turn confer elastomeric properties even when the crystalline block content is high. On the other hand, highly crystalline end blocks produce thicker, more-interconnected crystals, which lead to high moduli and yielding. Thus, any efforts to improve the mechanical performance of semicrystalline TPEs must address the morphology of the crystallites.

This chapter has shown in detail that adding glassy blocks to the block architecture is an effective way of limiting the crystallite size and improving the mechanical properties. However, since \((E-EP)_2\) is qualitatively elastomeric the improvements observed for the pentablocks appear modest. In contrast, the pentablock copolymers studied by Bishop and Register, which was the impetus for undertaking this work, provided enormous benefits over the comparable semicrystalline-rubbery-semicrystalline triblock.\(^{17}\) In their case, the crystalline block was hydrogenated polynorbornene (hPN), and the hPN-hPHN-hPN triblock exhibited plastic-like behavior with \(E_Y/E_N^0 = 20\), distinct yielding, and correspondingly high permanent set. Similar to LPE, hPN has a tendency to produce large, interconnected crystals and high degrees of
crystallinity. With this in mind, it becomes clear why the improvements afforded by the pentablock architecture were so striking.

Some comparisons can also be made between the pentablocks and other block copolymer architectures with semicrystalline and glassy blocks. Schmalz et al. studied S-EP-E triblocks with the intent of forming networks free from loops (i.e., where none of the chains have both end blocks in the same hard domain). Though the architecture was not designed explicitly to control the morphology of the crystallites, a triblock with \( w_S = 0.13 \) and \( w_E = 0.11 \) displayed a modest modulus ratio \( (E_Y/E_N) \approx 2.5 \) and good recovery \( (R_i \approx 96\%) \) up to failure. While this polymer performed well at low to moderate strains, the breaking strain was only \( \approx 300\% \), which was attributed to failure of the E crystallites. Bates and coworkers have studied a series of tough plastics comprising various linear sequences of E, C, and EP blocks. Though the total hard block contents were high (ca. 50\%) their results show that composite crystalline-glassy (either as C-E-C or C-E-C-E-C sequences) provided higher tensile strengths than E blocks alone when flanking a central EP block, particularly when the molecular weight was below about 100 kg/mol. These results bolster the conclusion that incorporating a load-bearing glassy block between the crystallites and the rubbery phase can thwart plastic deformation and improve the mechanical performance.
5.5 Conclusions

The phase behavior, thermal properties, rheology, and mechanical performance of four linear thermoplastic elastomers are presented. Two polymers with the pentablock architecture, crystalline-glassy-rubbery-glassy-crystalline, were compared against triblock copolymers having either crystalline or glassy end blocks at constant hard block content (20 wt%) and overall molecular weight ($M_n \approx 150$ g/mol). The triblock copolymer with glassy end blocks (C-EP)$_2$, which serves as a stand-in for commercial amorphous block copolymer TPEs, remains microphase-separated to at least 200 °C. As a consequence, the melt is highly viscous and shows substantial elastic character across the entire range of frequencies tested. The cylindrical glassy domains observed in the solid state confer a low Young’s modulus and the highest ultimate strength and recovery of the four polymers. The triblock with crystalline end blocks (E-EP)$_2$ was homogeneous above the melting point, and showed the lowest viscosity. However, in the solid state the lamellar crystals lead to higher moduli, poorer ultimate properties, and lower recovery.

The pentablock copolymers were designed to combine the processability advantages of the semicrystalline blocks while mitigating their negative impact on the mechanical performance. Small-angle x-ray scattering revealed that both pentablock copolymers (E-C-EP)$_2$-2 and (E-C-EP)$_2$-1 are indeed disordered above the melting point, proving the merits of the design strategy outlined in Chapter 4. Compared to the microphase-separated melt of (C-EP)$_2$, the viscosity of the pentablocks was reduced by over two orders of magnitude. When the pentablocks are cooled, crystallization begins to establish the network of physical cross-links before aggregation of the adjacent glassy blocks intervenes, limiting the size and connectivity of the crystallites, which in turn reduces the Young’s modulus. The vitreous layer which forms around the crystallites also improves the ultimate strength. Increasing the glassy block content provided
greater improvements in both the modulus and ultimate strength. Despite these improvements, the glassy blocks had little effect on the strain recovery values of the semicrystalline TPEs, which lie systematically below those of (C-EP)$_2$. When viewed in the context of prior work, the results presented here clearly demonstrate that the crystal morphology—specifically the size and connectivity of the crystals—is the most important parameter for controlling the mechanical properties. These results also demonstrate the general utility of the pentablock sequence as a simple architecture capable of producing TPEs which capture the advantages of both crystalline and glassy blocks.
5.6 References


Chapter 6

Effects of 6-Arm Star Architecture on the Performance of Block Copolymer Thermoplastic Elastomers

Compared to chemically cross-linked elastomers,\textsuperscript{1} high residual strain (permanent set) and dissipative loss (hysteresis), stemming from plastic deformation of the hard domains,\textsuperscript{2-6} remain significant drawbacks of TPEs. The previous chapter clearly showed that these shortcomings were more acute in TPEs with semicrystalline end blocks, and that incorporation of adjacent glassy blocks to create composite crystalline-glassy domains improves the stress-strain behavior but not the strain recovery. One way to further improve the mechanical performance of TPEs, irrespective of the type of hard domains, might be to use well-defined branched macromolecular architectures. The simplest and most common branched architecture is a star block copolymer comprising A-B arms with the B ends connected to a central core (denoted (A-B)\textsubscript{n}, where \(n\) is the number of arms). Commercially, star block copolymers with glassy end blocks (often referred to as “radial” block copolymers in the context of TPEs) are preferred in some applications where the block copolymer is blended with other components such as in thermoplastic toughening, pressure sensitive adhesives, and asphalt modification.\textsuperscript{7}

The properties of neat star block copolymers with glassy end blocks, prepared by a variety of methods, have also been studied in the literature.\textsuperscript{8-20} In many instances the neat star
block copolymers have been found to exhibit higher ultimate strengths ($\sigma_u$) than their linear analogs,\textsuperscript{9,19} which commonly comes at the expense of reduced breaking strains ($\varepsilon_b$).\textsuperscript{9,10,13,18,19} In instances where direct comparisons between linear and star block copolymers have been made, reports of both enhanced\textsuperscript{9} and diminished\textsuperscript{10} strain recovery (with respect to the corresponding linear polymers) can be found in the literature. Semicrystalline TPEs with well-defined branched architectures have not been studied in detail, but some evidence of improved recovery can nonetheless be found.\textsuperscript{21,22} Improvements in the mechanical properties in branched TPEs have been attributed to increased connectivity between the rubbery phase and the hard domains, which is better able to distribute stresses through the network.\textsuperscript{9,10} Moreover, the processability has been found to depend primarily on the composition and molecular weight of the arms, and only weakly on $n$ for $n \geq 3$.\textsuperscript{9,11,20}

In some cases, the contribution of the covalent cross-links is obscured by changes in the morphology arising from the architectural change,\textsuperscript{14} broad molecular weight (arm number) distributions,\textsuperscript{9,15,19} and non-negligible filler effects from the core of the star.\textsuperscript{9,16,19} Contributions from morphological changes and linking chemistry are avoided here by using precisely-defined 6-arm stars and well-matched arm molecular weight and composition to better understand the influence of the branch point on the mechanical response. Star polymers were prepared by sequential anionic polymerization, chlorosilane coupling, and catalytic hydrogenation as described in Chapter 4. A star functionality of six was chosen based on previous work\textsuperscript{9,10,12,13} demonstrating that the ultimate stress reaches a plateau in the range of $n = 5–10$. The core of the star is expected to function as a covalent cross-link which can distribute stress more uniformly and provide additional memory to the network without significantly altering the morphology or melt processability.\textsuperscript{9,11,19,20} This chapter reports results from a series of three star block polymers
having rubbery inner blocks and glassy, crystalline, or composite crystalline-glassy hard domains. The tensile properties and strain recovery behavior of the star block polymers are thoroughly characterized and compared with those of the well-matched linear block copolymers from Chapter 5.

6.1 Phase Behavior and Solid-State Structure

The morphology and phase behavior of the star block copolymers were characterized using SAXS and DSC. The derived characteristics are presented in Table 6.1 along with those of the relevant linear TPEs from Chapter 5. The SAXS patterns of (C-EP)$_2$ and (C-EP$_E$)$_6$ at room temperature and 200 °C are shown in Figure 6.1. The domain periodicities of (C-EP)$_2$ and (C-EP$_E$)$_6$ were found to be equal after heating to 200 °C and cooling to room temperature (Figure 6.1 and Table 6.1). As with (C-EP)$_2$, the lack of well-developed higher-order peaks in the SAXS patterns of (C-EP$_E$)$_6$ precluded a definitive morphological assignment. Based on self-consistent field theory predictions, the equilibrium morphology of (C-EP)$_2$ and (C-EP$_E$)$_6$ was expected to be hexagonally packed cylinders of C. The form factors for cylinders (Figure 6.2) and spheres (not shown) were calculated for (C-EP$_E$)$_6$ as described in Chapter 5 to aid in the assignment. The kink in the room-temperature scattering pattern near $q = 0.4$ nm$^{-1}$ agrees well with the first form factor minimum for cylinders (Figure 6.2). Additionally, the expected positions of the $\sqrt{3}$ and $\sqrt{4}$ peaks and the $\sqrt{7}$ and $\sqrt{9}$ peaks correspond to local maxima in the scattering pattern. Thus the morphology appears to be comparable to (C-EP)$_2$, namely cylindrical C domains with poor long-range order. Although the morphology and average periodicity between C domains was equivalent in the linear and star polymers, the morphology of (C-EP$_E$)$_6$ was somewhat less
regular, as evidenced by the broader primary SAXS peak. Both the linear and star block copolymers remained microphase-separated in the melt to at least 200 °C ($d = 38$ nm).

**Table 6.1.** Morphological and Thermal Characteristics of Linear and Star Block Copolymer TPEs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$d$ (nm)</th>
<th>$T_m$ (°C)</th>
<th>$t_c^a$ (nm)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$w_{c,E}^b$</th>
<th>$T_m$ (°C)</th>
<th>$t_c^a$ (nm)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$w_{c,E}^b$</th>
<th>$T_{g,EP}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-EP)$_2$</td>
<td>49</td>
<td>102</td>
<td>4.1</td>
<td>26.4</td>
<td>0.48</td>
<td>101</td>
<td>3.9</td>
<td>25.9</td>
<td>0.47</td>
<td>−59</td>
</tr>
<tr>
<td>(E-EP$_E$)$_6$</td>
<td>52</td>
<td>98</td>
<td>3.6</td>
<td>26.3</td>
<td>0.50</td>
<td>97</td>
<td>3.6</td>
<td>23.6</td>
<td>0.45</td>
<td>−58</td>
</tr>
<tr>
<td>(E-C-EP)$_2$-1</td>
<td>44</td>
<td>93</td>
<td>3.3</td>
<td>9.3</td>
<td>0.36</td>
<td>91</td>
<td>3.2</td>
<td>8.3</td>
<td>0.32</td>
<td>−59</td>
</tr>
<tr>
<td>(E-C-EP$_E$)$_6$-1</td>
<td>49</td>
<td>87</td>
<td>2.9</td>
<td>11.9</td>
<td>0.45</td>
<td>87</td>
<td>2.9</td>
<td>9.9</td>
<td>0.38</td>
<td>−58</td>
</tr>
<tr>
<td>(C-EP)$_2$</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−58</td>
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<tr>
<td>(C-EP$_E$)$_6$</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−58</td>
</tr>
</tbody>
</table>

$^a$Crystal thickness estimated from $T_m$ using the Gibbs-Thomson equation for crystallites of large lateral extent (equation [2.1]) with parameters$^{25}$ $T_m^0 = 141.9$ °C, $\Delta H_m,100 = 277$ J/g, and $\sigma = 55$ erg/cm$^2$. $^b$Apparent values calculated using equation [3.10].
Figure 6.1. SAXS patterns of (C-EP$_E$)$_6$ and (C-EP)$_2$ at room temperature (a) and at 200 °C (b).

The (C-EP$_E$)$_6$ patterns have been shifted up by a factor of 3 in intensity for clarity.
Figure 6.2. Room-temperature SAXS pattern of (C-EP_E)_6 (solid) with the form factor calculation for cylinders (R_{cyl} = 9.6 nm, dashed) and expected structure factor peak positions (triangles, q/q^* = 1, √3, √4, √7, √9).

The SAXS patterns of (E-EP_E)_6 showed a weak primary peak at low q followed by a broad region of intensity extending to higher q arising from the inter-crystallite spacing (Figure 6.3). As with (E-EP)_2, the morphology of (E-EP_E)_6 is established by crystallization and consists of clusters of E crystallites separated by regions of amorphous EP in an approximately lamellar arrangement with characteristic spacing d. The characteristic periodicity of (E-EP_E)_6 was 6% larger than that of (E-EP)_2, which is attributed to the slightly (16%) higher arm molecular weight in (E-EP_E)_6. Compared to (E-EP)_2, the SAXS pattern of (E-EP_E)_6 exhibited a weaker low-q feature, but higher intensity in the intermediate q-range (q = 0.2–0.8 nm\(^{-1}\)), indicative of a broader distribution of the crystal-amorphous spacing. The peak melting point of (E-EP_E)_6,
measured by DSC (Table 6.1 and Figure 6.4), was suppressed by 4 °C compared to (E-EP)₂, indicating that the crystals are somewhat thinner in the star polymer. The observed difference in the peak melting points does not stem from differences in the branch content of (E-EP)₂ and (E-EP₆)₆ (20.6 and 19.8 branches per 1000 backbone carbons, respectively), but rather is presumed to stem from retarded mobility of the star polymer during crystallization. On the other hand, the degree of crystallinity of the E blocks (w_{c,E}) was not strongly impacted by the star architecture (Table 6.1).
Figure 6.3. SAXS patterns of (E-EP_{6})_{6} and (E-EP)_{2} at room temperature (a) and at 110 °C (b).

The (E-EP_{6})_{6} pattern has been shifted up by a factor of 2 in intensity in (a) for clarity.
Figure 6.4. DSC traces of the semicrystalline linear and star TPEs on the first heating cycle (a) and subsequent cooling (b).
Access to homogeneous melts is a vital feature of the linear TPEs with composite crystalline-glassy hard domains, and must be maintained in star block polymers with the same motif, namely (crystalline-glassy-rubbery)_n. Theory\textsuperscript{28,29} predicts that the phase envelope (order-disorder transition, ODT) asymptotically shifts to lower arm molecular weight as the number of arms increases (i.e., the ordered state is stabilized by the star architecture), but that the dependence of the ODT on n is weak, a point which is corroborated by experiments.\textsuperscript{30,31} Thus, a single, judicious choice of block lengths should yield single-phase melts in both the linear and 6-arm star block polymers. Given the proximity of T_{ODT} to T_m in (E-C-EP)_2-1, a star polymer with the same composition (i.e., (E-C-EP)_6-1) provides a rather stringent test of this hypothesis.

The SAXS patterns of (E-C-EP)_6-1 exhibited correlation hole scattering (Figure 6.5b), which closely resembled the patterns of (E-C-EP)_2-1, indicating that the phase envelope had not shifted enough to qualitatively change the phase behavior in going from n = 2 to n = 6 (i.e., the order-disorder transition temperature still lies close to but below T_m). The solid-state SAXS pattern of (E-C-EP)_6-1 also resembled that of (E-C-EP)_2-1 (Figure 6.5a), though the characteristic spacing between composite crystalline-glassy domains was 10% larger in the former. DSC revealed that the T_m of (E-C-EP)_6-1 was 6 °C lower than in (E-C-EP)_2-1, but the apparent crystallinity of the E blocks was 20% higher in the star block copolymer. A portion of the observed endotherm is again attributed to the convolution of devitrification and dissolution of C block aggregates with the melting of the E crystallites. The differences in melting point (crystal thickness) and crystallinity again stem from the architecture and cannot be explained by differences in ethyl branch content, which are 20.1 per 1000 backbone carbons in (E-C-EP)_2-1 and 20.3 in (E-C-EP)_6-1. The increases in d and the apparent w_{c,E} observed in the star polymer may indicate that the C blocks are better segregated from E and EP in (E-C-EP)_6-1 than in (E-C-EP)_2-1.
EP)-1 following E block crystallization, resulting in purer, higher-$T_g$ C domains. The DSC cooling trace for (E-C-EP$_E)_6$-1 also lacks the well-developed, albeit small, crystallization peak near 70 °C observed in (E-C-EP)$_2$-1, meaning that crystallization is further hindered in the 6-arm star. These observations are consistent with a small quantitative shift in the ODT to lower segregation strength (higher temperature) with increasing $n$.

The results of the SAXS and DSC analyses show that in all three cases (glassy, crystalline, and composite hard domains) the phase behavior is not qualitatively altered by increasing $n$ from 2 to 6. In addition, the solid-state morphologies of the star polymers are similar to those of the corresponding linear polymers, save for small quantitative changes in the periodicity and regularity of the networks. Thus, differences in the mechanical properties between the star and linear TPEs (presented in the following sections) can be attributed to the covalent junction at the center of the star.
Figure 6.5. SAXS patterns of (E-C-EP$_6$)$_{1}$-1 and (E-C-EP)$_2$-1 at room temperature (a) and at 110 °C (b). The (E-C-EP$_6$)$_{1}$-1 pattern has been shifted up by a factor of 2 in intensity for clarity.
6.2 Tensile Properties

The most basic metrics of the mechanical performance, such as the Young’s modulus ($E_Y$) and the ultimate properties ($\varepsilon_b$, $\sigma_u$, and $T_u$), of TPEs are assessed using simple tensile tests. As mentioned above, many of the star block copolymers reported in the literature show improvements in these metrics as compared to their linear analogs, particularly the ultimate strength.\textsuperscript{9-19} Thus, the contribution of the star architecture is first evaluated by comparing the stress-strain curves of the 6-arm stars with the corresponding linear analogs.

The stress-strain curves for the linear and 6-arm star TPEs with glassy end blocks in uniaxial extension are shown in Figure 6.6. The average Young’s modulus ($E_Y$), ultimate strength ($\sigma_u$), breaking strain ($\varepsilon_b$), and ultimate toughness ($T_u$) measured therefrom are listed in Table 6.2. At small strains the linear and star polymers behaved similarly since the response is dominated by trapped entanglements (the entanglement molecular weight for EP\textsubscript{32} is $\approx$1.5 kg/mol) and the volume fraction and morphology of the C domains, which was minimally impacted by the change in architecture. The variability in the modulus of (C-EP\textsubscript{2})\textsubscript{2}, which was attributed to differences in the alignment of the cylindrical domains with respect to the stretching direction,\textsuperscript{2,4,33} was not observed for (C-EP\textsubscript{E})\textsubscript{6}. Above about 50% strain, (C-EP\textsubscript{E})\textsubscript{6} exhibited more pronounced strain hardening than (C-EP\textsubscript{2}), and $\sigma_u$ was increased by a factor of 1.3, while $\varepsilon_b$ was 140% lower on average. These results are consistent with previous reports on star block copolymer TPEs with glassy end blocks.\textsuperscript{9,10,13,18,19} Comparing the best-performing specimens of each material suggests that the true enhancement might be even greater, but the intrinsic ultimate properties are difficult to measure experimentally due to premature failure induced by impurities. Interestingly, the energy (per unit volume of deformed material) required to break the specimen (i.e., the ultimate toughness) of the linear and star polymers were equal (Table 6.2).
Figure 6.6. Stress-strain curves for (C-EP\textsubscript{6})\textsubscript{6} and (C-EP)\textsubscript{2}.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_Y^a$ (MPa)</th>
<th>SD\textsuperscript{b} (%)</th>
<th>$E_Y/E_N^0$</th>
<th>$\sigma_u$ (MPa)</th>
<th>SD\textsuperscript{b} (%)</th>
<th>$\varepsilon_b$ (%)</th>
<th>SD\textsuperscript{b} (%)</th>
<th>$T_u$ (MJ/m\textsuperscript{3})</th>
<th>SD\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-EP)\textsubscript{2}</td>
<td>10.2</td>
<td>2</td>
<td>2.9</td>
<td>6.4\textsuperscript{c} / 6.4\textsuperscript{a}</td>
<td>1</td>
<td>570\textsuperscript{c} / 560\textsuperscript{a}</td>
<td>1</td>
<td>19.0\textsuperscript{c} / 19\textsuperscript{a}</td>
<td>1</td>
</tr>
<tr>
<td>(E-EP)\textsubscript{6}</td>
<td>10.5</td>
<td>5</td>
<td>3.1</td>
<td>8.2 / 7.7</td>
<td>8</td>
<td>580 / 540</td>
<td>6</td>
<td>23.7 / 21</td>
<td>14</td>
</tr>
<tr>
<td>(E-C-EP)\textsubscript{2}-1</td>
<td>6.7</td>
<td>4</td>
<td>1.9</td>
<td>8.4 / 6.9</td>
<td>20</td>
<td>740 / 660</td>
<td>15</td>
<td>29.1 / 22</td>
<td>31</td>
</tr>
<tr>
<td>(E-C-EP)\textsubscript{6}-1</td>
<td>7.1</td>
<td>6</td>
<td>2.1</td>
<td>8.9 / 7.3</td>
<td>19</td>
<td>620 / 540</td>
<td>13</td>
<td>26.3 / 20</td>
<td>27</td>
</tr>
<tr>
<td>(C-EP)\textsubscript{2}</td>
<td>7.1</td>
<td>34</td>
<td>2.1</td>
<td>11.0\textsuperscript{d} / 9.6</td>
<td>21</td>
<td>850\textsuperscript{d} / 800</td>
<td>7</td>
<td>34.1\textsuperscript{d} / 29</td>
<td>22</td>
</tr>
<tr>
<td>(C-EP)\textsubscript{6}</td>
<td>7.3</td>
<td>5</td>
<td>2.1</td>
<td>16.5 / 12.8</td>
<td>36</td>
<td>700 / 660</td>
<td>9</td>
<td>34.4 / 28</td>
<td>27</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Average and \textsuperscript{b}one standard deviation of at least 3 specimens, \textsuperscript{c}maximum measured value; for (C-EP)\textsubscript{2} the maximum $\sigma_u$, $\varepsilon_b$, and $T_u$ were measured in three different specimens, for all other polymers the maximum values were measured in a single specimen.
The stress-strain curves for \((E\text{-}EP_E)_6\) and \((E\text{-}EP)_2\) are shown in Figure 6.7. The Young’s moduli of the star and linear polymers were equal within experimental uncertainty (Table 6.2). In spite of the reduced crystal thickness, which is expected to make the crystals more susceptible to plastic deformation, \((E\text{-}EP_E)_6\) was actually stiffer than \((E\text{-}EP)_2\) above \(\approx 50\%\) strain, culminating in an average increase in \(\sigma_u\) by a factor of 1.2, with no change in \(\varepsilon_b\). The best-performing sample of \((E\text{-}EP_E)_6\) also showed a factor of 1.2 increase in toughness. Interestingly, the failure mechanism of \((E\text{-}EP_E)_6\) was notably different that the other TPEs. Whereas all of the other TPEs failed catastrophically (i.e., failure was nearly instantaneous), \((E\text{-}EP_E)_6\) failed via relatively slow propagation of a tear. The resulting stress-strain curves had a region of reduced strain hardening followed by a maximum in the stress, after which the stress decreased with increasing strain (not shown) as the tear propagated through the specimen (the ultimate properties in Table 6.2 correspond to the point of maximum stress). While \((E\text{-}EP)_2\) also showed evidence of decreased strain hardening immediately prior to failure, the specimens appear to the naked eye to fail catastrophically.
Figure 6.7. Stress-strain curves for \((E-EP_{E})_6\) and \((E-EP)_2\).

The stress-strain response of \((E-C-EP_{E})_6\)-1 is compared with that of \((E-C-EP)_2\)-1 in Figure 6.8. As with \((C-EP_{E})_6\) and \((E-EP_{E})_6\), the small-strain behavior of \((E-C-EP_{E})_6\)-1 closely mirrored that of its linear analog. At moderate strains, \((E-C-EP_{E})_6\)-1 was stiffer than \((E-C-EP)_2\)-1, again consistent with the behavior of the TPEs with purely glassy or purely crystalline end blocks. The enhanced stiffness of \((E-C-EP_{E})_6\)-1 did not result in a significant improvement in \(\sigma_u\), and the differences in \(\varepsilon_b\) and \(T_u\) were well within the uncertainty of the measurement. Again, the true ultimate properties can be difficult to measure experimentally, so it is unclear whether this behavior is intrinsic.
6.3 Strain Recovery

Though the tensile properties of the star polymer TPEs are commonly reported in the literature, detailed reports on the strain recovery behavior are comparatively rare, particularly for semicrystalline TPEs. However, this aspect of the mechanical response requires the most improvement if TPEs are to truly compete with vulcanized rubbers. One of the primary goals of this work is to determine whether the star macromolecular architecture is a viable option for increasing the recovery (reducing the permanent set) in block copolymer TPEs based on crystalline, glassy, or composite hard domains. In this section the strain recovery is measured using the cyclic strain test introduced previously. The influence of the star architecture is again assessed by comparing the performance of the stars to their linear counterparts.
The initial and final cyclic recovery behavior of (C-EP\(_E\))\(_6\) compared to (C-EP)\(_2\) is shown in Figure 6.9. The star architecture clearly provided enhanced recovery across the range of \(\varepsilon_a\) investigated, both in \(R^i\) and \(R^f\). In addition to a more even distribution of stresses, the permanent cross-link at the core of the star evidently provides additional memory to the network. Unlike the stress-strain behavior, the improvement in the strain recovery of (C-EP\(_E\))\(_6\), relative to (C-EP)\(_2\), diminished as the strain increased. Unfortunately the recovery of (C-EP\(_E\))\(_6\) could not be accurately determined at \(\varepsilon_a = 500\%\) because the specimens slipped in the grips during testing. At these large strains the glassy domains have undergone substantial restructuring,\(^{2,4}\) which dominates the residual strain and apparently reduces the ability of the permanent cross-link to restore the initial state. As a point of comparison, the recovery of (C-EP)_2 was on par with Kraton\(^{®}\) D1111, a commercial styrenic triblock copolymer TPE. Kraton\(^{®}\) D1111 is a polystyrene-polyisoprene-polystyrene (S-I-S) triblock copolymer with 20 vol% S (compared to 18.4 vol% C in (C-EP)_2 and 17.8 vol% C in (C-EP\(_E\))\(_6\), at 20 °C),\(^{34}\) \(M_n \approx 130\) kg/mol, and approximately 19% diblock.\(^{35}\) Despite differences in the \(T_g\) values and entanglement molecular weights of the constituent blocks and the segregation strength, D1111 and (C-EP)\(_2\) perform similarly.
Figure 6.9. Initial (a) and final (b) recovery of \((\text{C-EP}_E)_6\), \((\text{C-EP})_2\), and Kraton\textsuperscript{®} D1111.
The 6-arm star with crystalline hard domains outperformed the linear polymer in initial recovery (Figure 6.10). Similar to the polymers with glassy end blocks, the difference between (E-EP)\textsubscript{2} and (E-EP\textsubscript{E})\textsubscript{6} diminished as $\varepsilon_a$ increased until the recovery was essentially equal for $\varepsilon_a \geq 400\%$. The recovery benefits of the star architecture also diminished after the samples were allowed to rest for 5 min (Figure 6.10b). Both the linear and star polymers ultimately recovered to nearly the same degree; however, (E-EP\textsubscript{E})\textsubscript{6} recovered more quickly, with only ca. 2% of additional recovery during the 5 min rest, while (E-EP)\textsubscript{2} recovered nearly twice as much over the same period. These results imply that the covalent cross-link at the center of the star facilitates rapid recovery of the (visco)elastic deformation, but does not dramatically suppress the plastic deformation mechanisms which contribute to permanent set. It is noteworthy that (E-EP\textsubscript{E})\textsubscript{6} outperformed (E-EP)\textsubscript{2}, if only modestly, in spite of the reduced crystal thickness; even better performance might be achieved by tuning the crystallization conditions to obtain comparable crystal thicknesses. Comparing the recovery of (E-EP)\textsubscript{2} and (E-EP\textsubscript{E})\textsubscript{6} to those of (C-EP)\textsubscript{2} and (C-EP\textsubscript{E})\textsubscript{6} (cf. Figure 6.9), the latter of which were significantly higher, illustrates the adverse effects of plastic deformation in the crystalline domains. (E-C-EP\textsubscript{E})\textsubscript{6}-1 also showed better initial recovery than (E-C-EP)\textsubscript{2}-1 (Figure 6.10a). Interestingly, $R'$ was also higher for (E-C-EP\textsubscript{E})\textsubscript{6}-1 than the corresponding linear polymer (Figure 6.10b), particularly at the lowest $\varepsilon_a$, despite the finding that neither (E-C-EP)\textsubscript{2}-1 nor (E-EP\textsubscript{E})\textsubscript{6} provided significantly better performance than (E-EP)\textsubscript{2}. The apparent synergistic effects of the glassy blocks and the star architecture may be explained by the formation of more robust C domains in (E-C-EP\textsubscript{E})\textsubscript{6}-1 inferred from the increases in $d$ and the apparent $w_{c,E}$.  

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Figure 6.10. Initial (a) and final (b) recovery of $(E-EP_E)_6$ and $(E-EP)_2$. 
Figure 6.11. Initial (a) and final (b) recovery of (E-C-EP$_E$)$_6$-1 and (E-C-EP)$_2$-1.
6.4 Hysteresis

In addition to the recovery, another quantitative metric for elasticity is fractional hysteresis ($H$), which measures the amount of energy dissipated during deformation as heat.\textsuperscript{1,36} It is desirable to minimize hysteresis in elastomers. This is particularly important for applications where the material is subjected to cyclic deformation (such as tires) because the heat generated in each cycle due to hysteretic loss can build up causing the temperature of the specimen to rise. This can become intractable for TPEs, where the physical cross-linking domains soften at elevated temperatures.

The fractional hysteresis was calculated from the same cyclic strain data used to compute the recovery. Figure 6.12 shows $H$ as a function of $\varepsilon_a$ for the all-amorphous TPEs. The hysteresis behavior of (C-EP)$_2$ was complicated by the influence of the morphology. As mentioned previously, the mechanical properties of (C-EP)$_2$ are sensitive to the degree of alignment between the microdomains and the stretching direction. The initial modulus of the three specimens used for cyclic testing ranged from 6.6 to 28.7 MPa, and the concomitant changes in the shape of the stress-strain curve\textsuperscript{2,4,33} resulted in large variability in $H$ (specimens with higher $E_Y$ exhibited more hysteresis). Nevertheless, the hysteresis of (C-EP)$_2$ was remarkably similar to that of Kraton® D1111. Interestingly, the shape of the cyclic stress-strain curves of (C-EP)$_2$ did not greatly impact the recovery, as evidenced by the comparatively small error bars in Figure 6.9. (C-EP)$_6$ showed no evidence of alignment ($E_Y = 7.3$–$8.2$ MPa for the three specimens tested), and there was correspondingly less variability in $H$. If all of the samples of (C-EP)$_2$ were considered, the star architecture reduced $H$ by 30%. (C-EP)$_6$ had slightly more hysteresis than the best-performing specimen of (C-EP)$_2$ at small strains ($\varepsilon_a \leq 50\%$), but still performed better by a factor of 1.2 for $\varepsilon_a \geq 100\%$. 

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Figure 6.12. Fractional hysteresis of (C-EP)$_2$, (C-EP)$_6$, and Kraton$^\text{®}$ D1111, including both the best-performing specimen and average of three specimens of (C-EP)$_2$.

Turning to the semicrystalline polymers (Figures 6.13 and 6.14), the hysteresis of (E-EP)$_2$ agreed well with prior measurements on an E-EP-E triblock with 18 wt% E. The hysteresis of (E-EP)$_6$ was reduced by a factor of 1.5 with respect to that of (E-EP)$_2$ for $\varepsilon_a \leq 200\%$. Similar behavior was observed for (E-C-EP)$_6$-1, which showed a factor of 1.3 reduction in $H$ compared to its linear counterpart (E-C-EP)$_2$-1 for $\varepsilon_a \leq 200\%$. In the range $\varepsilon_a = 300$–$400\%$, $H$ for the semicrystalline stars and the corresponding linear polymers were comparable, and at $\varepsilon_a = 500\%$ the linear polymers showed less hysteresis. The initial recovery showed a similar trend, namely the improvements exhibited by the 6-arm star diminished as $\varepsilon_a$ increased. However, the stars always performed at least as well as the corresponding linear polymer, and in the case of the composite hard domains (E-C-EP)$_6$-1 exhibited better $R^\text{f}$ across the entire range of $\varepsilon_a$. For
comparison, \( H \approx 0.2 \) at \( \varepsilon_a = 100\% \) for vulcanized natural rubber (NR) and styrene-butadiene rubber (SBR) with 20 wt\% filler.\(^{36}\) It bears mentioning that the hysteresis of vulcanized rubber depends strongly on the filler content \( (H \approx 0.05 \) for unfilled NR and 0.1 for unfilled SBR), cross-linking density, and testing rate. Nevertheless, all three star polymers studied here provided hysteresis performance which is competitive with that of filled vulcanized rubbers. Furthermore, the improvements in \( H \) associated with the star architecture are comparable to improving \( H \) in vulcanized rubber by reducing the filler fraction. However, changing the filler fraction changes \( E_Y \),\(^{38}\) whereas the star TPEs studied here did not.
Figure 6.13. Fractional hysteresis of (E-EP)_2 and (E-EP_E)_6.

Figure 6.14. Fractional hysteresis of (E-C-EP)_2-1 and (E-C-EP_E)_6-1.
6.5 Role of the Star Architecture and Comparison with Literature

It is clear that the star architecture in an effective way to improve the mechanical performance of TPEs, but the property which was most improved and the degree of improvement was found to vary depending on the identity of the hard blocks. During the initial deformation (less than 50% strain) entanglements dominate and the contribution of the core of the star is minimal, hence $E_Y$ changes very little. At moderate and large strains, the role of the covalent junction at the core of the star is to more effectively distribute stresses to the hard domains,\textsuperscript{9,10} which makes the stars stiffer than the corresponding linear polymers at any given strain (above \approx 50% strain). In this regime, chain pullout and deformation of the hard domains is expected to limit the recovery, contribute to the hysteresis, and ultimately lead to failure for all of the polymers studied here.\textsuperscript{5,39-41} The role of the star architecture is to maintain elastically effective connections between the rubbery phase and the hard domains in spite of these processes. If a hard block becomes detached from its corresponding domain (by pullout, scission, or domain rupture) the triblock copolymer can relax completely, releasing trapped entanglements and contributing to the hysteresis and permanent set (Figure 6.15a). In the case of the star block copolymer only the failed arm can relax (releasing only half as many entanglements as in the triblock if the arm molecular weight is equivalent) while the intact arms remain anchored to the network (Figure 6.15b), leading to less hysteresis and better recovery.
The same argument holds regardless of the type of hard domain (glassy, crystalline, and composite). The purely crystalline end blocks are the most prone to plastic deformation and thus show improvements in the rate of recovery ($R'$) and the hysteresis, but not the final recovery. As with the linear polymers, the addition of the adjacent glassy blocks (to form composite crystalline-glassy hard domains) lowered the modulus of (E-C-EP$_E$)$_6$-1 compared to (E-EP$_E$)$_6$, due to a reduction in the crystallite size and connectivity. The measured ultimate properties of (E-C-EP$_E$)$_6$-1 and (E-EP$_E$)$_6$ were quite similar, unlike the linear polymers where the ultimate properties were improved by the presence of the glassy blocks. Despite this, (E-C-EP$_E$)$_6$-1
showed better recovery than (E-EP\(_E\))\(_6\) at low to moderate strains indicating that the composite E-C domains were more robust than the bare E crystallites in the 6-arm stars. However, the modest improvements indicate that plastic deformation of the crystals still limits the performance. Consequently, the benefits of the star architecture are greatest when the end blocks are glassy.

The significance of the improvements in elastic response observed for the star polymers studied here can be contextualized by comparing them to other branched TPEs for which equivalent data are available. Star block copolymers with S hard blocks and I rubbery blocks studied by Bi and Fetters showed similar trends in \(\sigma_u\) and \(\varepsilon_b\) compared to (C-EP\(_E\))\(_6\), as noted above.\(^9\) The recovery behavior was not studied in detail; however, the authors noted that the permanent set of the star block copolymers was reduced by a factor of 5 compared to the linear analogs, and the recovery of the (S-I)\(_n\) stars was as high as \(R' \geq 98\%\). Shim and Kennedy also reported increases in \(\sigma_u\), but found a deleterious effect of the star architecture on the permanent set.\(^10\) Staudinger et al. studied a series of multigraft copolymers comprising I backbones with regularly spaced S grafts.\(^{42}\) The multigrafts exhibited \(\varepsilon_b > 1200\%\), but had weaker strain hardening and lower \(\sigma_u\) compared to a commercial S-I-S triblock copolymer, in contrast to the star block polymers studied here and by others.\(^9\)\(^{-19}\) A polymer with similar hard block composition (17 vol% S) to (C-EP)\(_2\) and (C-EP\(_E\))\(_6\) and 3.7 grafts per chain (with one S chain per graft point) exhibited \(R' \approx 93\%\), less than even (E-EP)\(_2\). A graft polymer with 22 vol% S and 5.2 grafts per chain (with four S chains per graft point) had \(R' \approx 95\%\), compared to \(R' > 97\%\) for (C-EP\(_E\))\(_6\). This graft copolymer also showed considerable hysteresis, although \(H\) was not quantified.

While studies of semicrystalline TPEs are comparatively rare, some architectures more complex than triblocks have been reported. Kong et al. demonstrated that a 4-arm star\(^{21}\) with 22 wt% semicrystalline poly(l-lactide) end blocks recovered >10% more than its linear analog\(^{22}\) (\(\varepsilon_a\)
= 150%), but $R^f$ was still less than 85%. Coates and coworkers have reported a series of linear multiblock copolymers having alternating crystalline and amorphous blocks.\textsuperscript{43,44} They found that substantial improvements in $\sigma_u$ can result from having central crystalline blocks flanked by rubbery blocks (e.g., $i$PP-$r$PP-$i$PP-$r$PP-$i$PP versus $i$PP-$r$PP-$i$PP\textsuperscript{43} where $r$PP and $i$PP are rubbery regioirregular and crystalline \textit{isotatic} polypropylene, respectively); however, the recovery of the multiblocks was comparable if not somewhat worse than for the triblocks.\textsuperscript{43,44} Graft copolymers with EP backbones (synthesized by copolymerizing ethylene and propylene) and crystalline tactic PP grafts provided similar improvements in $R^f$ compared to the conventional triblock architecture as the 6-arm stars studied here. A graft copolymer with \textit{syndiotactic} PP hard blocks showed an increase in $R^f$ by almost 20\% (at $\varepsilon_d = 500\%$) over an $s$PP-EP-$s$PP triblock copolymer, which suffered from considerable permanent set. However, the best-performing graft copolymers had $R^f \approx 90\%$, lower than $(E$-EP)$_2$ and $(E$-EP)$_6$.\textsuperscript{45} Determining the contribution of the graft architecture is also complicated by the fact that the hard block fraction in the grafts was <10 wt\%, compared to 24 wt\% in the triblocks.
6.6 Conclusions

In conclusion, using a star macromolecular architecture improved the ultimate strength, strain recovery, and hysteresis of block polymer thermoplastic elastomers with glassy, crystalline, and composite crystalline-glassy physical cross-links. The star architecture did not qualitatively alter the network morphology or phase behavior in any of the three cases studied. As a result, stress-strain curves for the 6-arm star polymers were almost indistinguishable from those of their linear analogs at small strains. At moderate and high strains the core of the star acts as a permanent cross-link, which distributes stresses more evenly and provides additional memory to the network, resulting in enhanced stiffness and recovery. The improvements were most pronounced when the hard domains were entirely glassy. Interestingly, the star TPE with purely crystalline hard domains exhibited higher ultimate stresses and recovered at least as well as its linear analog despite having somewhat thinner crystals. The behavior of the star TPE with composite hard domains was similar although $\sigma_u$ was equal to that of the linear analog. The covalent cross-link accelerated recovery and reduced the hysteresis during cyclic strain in the semicrystalline materials. (E-EP$_E$)$_6$ showed minimal improvements in the final set compared to (E-EP)$_2$, which is dictated by plastic deformation of the crystallites. On the other hand, the final recovery of (E-C-EP$_E$)$_6$-1 was higher than any of the other semicrystalline TPEs, despite the fact that the composite hard domains or the star architecture alone failed to increase the recovery. In comparison with other branched architectures reported in the literature, these findings underscore the utility of using well-defined star block copolymers to enhance strain hardening and increase recovery in block polymer TPEs.
6.7 References


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Chapter 7

Lamellar Forming Crystalline-Rubbery Diblock Copolymers

The phase behavior and morphology of block copolymers containing crystallizable blocks is determined by the complex interplay between crystallization and block incompatibility. To this point this thesis has focused on materials in which the solid-state structure is driven by crystallization from a disordered melt. This chapter deals with the other end of the spectrum. Namely, crystalline-amorphous diblock copolymers are investigated in which the morphology is established by block incompatibility in the melt, and crystallization is restricted to the crystallizable microdomains. Crystallization can be confined within block copolymer microdomains using one of two strategies: (1) using amorphous blocks which are glassy when crystallization occurs,1-10 or (2) using strongly segregated (high $\chi N$) pairs of blocks.11-14

Many aspects of confined crystallization within block copolymer microdomains have been elucidated; however, some questions remain unanswered. The relationship between the crystallite orientation and size and the microdomain morphology is well understood when the crystallizable microdomains are isolated (i.e., spherical or cylindrical domains of the crystallizable component in an amorphous matrix). Crystallization in spheres is equally constrained in all three dimensions and thus the crystal orientation is essentially isotropic and the crystallite size is severely limited.3,9 In cylinders, where crystallization is confined in the radial
direction but relatively unconstrained in the axial direction, the fast growth direction of the crystals is typically coincident with the cylinder axis.$^{3,4,9}$

A variety of scenarios can arise for crystallization in lamellar microdomains because the crystallites are constrained in the direction normal to the microdomain interfaces but unconstrained in the two orthogonal directions. The interconnectivity between crystallizable lamellae (via grain boundaries and dislocations)$^{15,16}$ allows crystallization to proceed via heterogeneous nucleation irrespective of the degree of confinement, in contrast with spherical and cylindrical morphologies where the microdomains must undergo homogeneous nucleation.$^{10-13}$ The resulting crystal texture is established by the tradeoff between several factors. In general, thicker crystals are more stable,$^{17}$ so crystal orientations within the microdomains which severely limit the crystal thickness are disfavored. However, the block junction must remain anchored to the domain interface and both the amorphous and crystalline blocks must occupy the same interfacial area per chain,$^{18}$ which must ultimately limit the crystal thickness. This is a non-trivial matter given that the chain conformations on either side of the interface are very different—the amorphous chains adopt Gaussian conformations at equilibrium, while the crystal stems are locally extended. As a result, the minimum free energy state for the crystals in the block copolymer differs from that in the bulk semicrystalline homopolymer (where the equilibrium structure is the extended-chain crystal) and is difficult to predict $a$ priori.

Most of the work to date has made use of either hydrogenated high 1,4-polybutadiene (linear low-density polyethylene, E) or poly(ethylene oxide) (EO). While the former is attractive from a synthetic standpoint, the crystal thickness is inherently limited by ethyl branches$^{19,20}$ and thus is essentially independent of the block copolymer morphology. Nonetheless, under lamellar confinement E crystallites orient with the crystal stems ($c$-axis) and fast growth direction ($b$-axis)
parallel to the domain interface, with free rotation about the lamellar normal \((a\text{-axis})\).\textsuperscript{3} The same arrangement was observed in linear polyethylene (LPE) under hard confinement,\textsuperscript{9} confirming the hypothesis that this orientation is preferred because it allows the crystal thickness to exceed the LPE layer thickness. In diblock copolymers containing EO under hard confinement, the crystal orientation has been found to depend on the crystallization conditions\textsuperscript{6-8} and the size of the EO domains.\textsuperscript{8} As the degree of undercooling increases, the orientation of the crystal stems with respect to the microdomain interfaces changes smoothly from normal to parallel.\textsuperscript{6-8} When quenched in liquid nitrogen, the EO crystallites show no preferred orientation. This progression reflects the increase in nucleation density with increasing undercooling.\textsuperscript{6,7}

This work seeks to further understand the impact of soft lamellar confinement on the crystallite orientation and size in crystalline-amorphous diblocks. The crystallizable block is hydrogenated atactic polynorbornene\textsuperscript{21} (hPN). hPN offers several attractive features: (1) it is readily incorporated into block copolymers using ring-opening metathesis polymerization (ROMP), (2) it crystallizes rapidly and is highly crystalline, and (3) hPN crystallites transform to a rotationally disordered crystalline phase\textsuperscript{21,22} prior to melting, wherein the crystals undergo rapid thickening.\textsuperscript{22} These characteristics are well-suited for studying crystallization in block copolymer microdomains. Though a myriad of norbornene monomers bearing hydrocarbon substituents are available,\textsuperscript{23-25} the structural similarity between various polymers in this family leads to low \(\chi\) against hPN. Regardless of whether the amorphous block glass transition temperature \((T_g)\) is greater than the melting temperature \((T_m \approx 140 \, ^\circ\text{C} \text{ for hPN})\), these amorphous blocks are ill-suited for studying confined crystallization because robust microdomains cannot be formed over a range of molecular weights. The amorphous component of choice for this work is
thus the recently reported\textsuperscript{26} hydroxyhexafluoroisopropyl substituted norbornene (HFAN) whose polar side group was expected to yield a large $\chi$ against hPN.

\textbf{7.1 Synthesis of hP(N-HFAN) Diblock Copolymers}

The polymers described in this chapter were prepared by ring-opening metathesis polymerization (ROMP) followed by catalytic hydrogenation. The monomers norbornene (N) and hydroxyhexafluoroisopropylnorbornene (2-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1,1,3,3,3-hexafluoropropan-2-ol) were polymerized using the 1\textsuperscript{st} Generation Grubbs initiator in the presence of 5 molar equivalents of tricyclohexylphosphine. Diblock copolymers were prepared by polymerizing the N block first to avoid inclusion of the slowly polymerizing HFAN units, which would subsequently act as defects in the crystallizing hPN block. The compositions were determined by $^1$H NMR spectroscopy in THF-$d_8$ (see Figure 7.1). The $^1$H NMR spectra of polymers containing HFAN depend strongly on the choice of deuterated solvent; in addition to being a good solvent for both blocks, THF-$d_8$ produce a clearly resolved hydroxyl peak, making the analysis straightforward. The molecular weights and distributions were characterized by GPC using $dn/dc = 0.1549$ mL/g and $r = 2.06$ for PN and $dn/dc = 0.0385$ mL/g and $r = 1.29$ for PHFAN; Figure 7.2 shows a representative example. Table 7.1 contains the relevant molecular characteristics of the as-synthesized polymers.
Figure 7.1. $^1$H NMR spectrum of the unsaturated precursor to hP(N-HFAN)-43 collected in THF-d$_8$ showing the hydroxyl (H$_a$) and olefinic (H$_b$) peaks.

Figure 7.2. GPC traces of the PN 1$^{st}$ block and unsaturated diblock precursor to hP(N-HFAN)-25.
Table 7.1. Molecular Characteristics of As-Synthesized Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>1st Block</th>
<th>Diblock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{LS}$ (kg/mol)</td>
<td>$M_{n,r}$ (kg/mol)</td>
</tr>
<tr>
<td>hPHFAN-41</td>
<td>46.8</td>
<td>40.5$^a$</td>
</tr>
<tr>
<td>hP(N-HFAN)-17</td>
<td>9.6</td>
<td>9.5</td>
</tr>
<tr>
<td>hP(N-HFAN)-25</td>
<td>14.2</td>
<td>14.5</td>
</tr>
<tr>
<td>hP(N-HFAN)-43</td>
<td>21.1</td>
<td>21.1</td>
</tr>
<tr>
<td>hP(N-HFAN)-69</td>
<td>36.5</td>
<td>36.1</td>
</tr>
</tbody>
</table>

$^a$hPHFAN-41 was used to calculate $r = M_{n,PS}/(M_{LS}/\mathcal{D}) = 1.29$, and $M_{n,r} = M_{n,PS}/r = M_{LS}/\mathcal{D}$.

The amphiphilic nature of the P(N-HFAN) diblock copolymers polymers made isolation by precipitation challenging. The block copolymers were isolated by precipitation in hexanes or a 1:1 v/v mixture of methanol and water, dried in a vacuum oven, and stored in a freezer. The polymers were characterized again immediately prior to saturation (Table 7.2), which revealed some changes in the molecular weight distributions. Precipitation removed the low molecular weight tail from the precursor to hP(N-HFAN)-43, reducing $\mathcal{D}$. The molecular weight distributions of the precursors for hP(N-HFAN)-17 and -25 developed low molecular weight tails during workup and storage. The polymers were saturated over Pd/CaCO$_3$. FTIR was not sensitive enough to quantify the degree of saturation because the characteristic trans C=C peak at 966 cm$^{-1}$ could not be adequately resolved. Instead, the progress of the reaction was monitored by room temperature $^1$H NMR. $^1$H NMR is not ideal for this purpose because hPN is not fully soluble; however, the unsaturated units, particularly in the amorphous block, are nonetheless well represented. The saturated diblock copolymers are identified by their constituent blocks followed by the diblock molecular weight ($M_{n,r}$) in kg/mol (after adding 2 g/mol per repeat unit to account for hydrogenation). The weight fractions ($w$), measured by $^1$H
NMR on the unsaturated precursors, were converted to volume fractions \( (\phi) \) using specific volume correlations for the homopolymers.\(^{27,28}\)

### Table 7.2. Molecular Characteristics of hPHFAN and hP(N-HFAN) Diblocks\(^a\)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_{LS} ) (kg/mol)</th>
<th>( M_{n,r} ) (kg/mol)</th>
<th>( D )</th>
<th>( w_{hPN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPHFAN-41</td>
<td>47.1</td>
<td>40.8(^b)</td>
<td>1.16</td>
<td>0</td>
</tr>
<tr>
<td>hP(N-HFAN)-17</td>
<td>21.0</td>
<td>17.3</td>
<td>1.43</td>
<td>0.431</td>
</tr>
<tr>
<td>hP(N-HFAN)-25</td>
<td>30.3</td>
<td>24.7</td>
<td>1.43</td>
<td>0.426</td>
</tr>
<tr>
<td>hP(N-HFAN)-43</td>
<td>45.9</td>
<td>42.9</td>
<td>1.14</td>
<td>0.456</td>
</tr>
<tr>
<td>hP(N-HFAN)-69</td>
<td>78.7</td>
<td>69.0</td>
<td>1.22</td>
<td>0.454</td>
</tr>
</tbody>
</table>

\(^a\)Characterization of the unsaturated precursors immediately prior to hydrogenation and adjusted for the addition of 2 g/mol per repeat unit upon saturation. \(^b\)hPHFAN-41 was used to calculate \( r = \frac{M_{n,PS}}{M_{LS}/D} = 1.29 \), and \( M_{n,r} = \frac{M_{n,PS}}{r} = \frac{M_{LS}}{D} \).

### 7.2 Phase Behavior and Morphology

The thermal behavior of the diblock copolymers was characterized by differential scanning calorimetry (DSC). The DSC traces on heating and cooling are shown in Figure 7.3; the thermal characteristics measured on heating are given in Table 7.3. The peak melting temperatures \( (T_m) \) are similar to that of homopolymer hPN synthesized under the same conditions.\(^{22}\) The degrees of crystallinity of the hPN blocks \( (w_{c,hPN}) \) are \( \approx 15\% \) less than that of hPN homopolymer in all but the lowest molecular weight diblock. The small endotherm associated with the polymorphic transition\(^{21,22}\) from the rotationally ordered, monoclinic unit cell to the rotationally disordered pseudohexagonal crystal structure \( (T_{cc}) \) was resolvable on heating, except in hP(N-HFAN)-25. hP(N-HFAN)-25 also exhibited bimodal crystallization (Figure 7.3b). This behavior may be attributable to two populations of microdomains, one which is which is nucleated heterogeneously (smaller undercooling) and the other which is
homogeneously nucleated (larger undercooling). All four polymers showed clear hPHFAN glass transition temperatures ($T_g$) in good agreement with that of the homopolymer (see Appendix A for DSC trace of hPHFAN-41), indicating that the hPHFAN blocks are well segregated from the amorphous hPN. Given that the hPHFAN blocks are rubbery when the hPN blocks crystallize (Figure 7.3b), the crystals (if confined) are subject to “soft” confinement, and the rubbery domains are able to accommodate the volume change on crystallization.
Figure 7.3. DSC traces of hP(N-HFAN) diblock copolymers on heating (a) and cooling (b) at 10 °C/min.
Table 7.3. Thermal Characteristics of hPHFAN and hP(N-HFAN) Diblocks

| Polymer          | $T_g$ (°C) | $T_{cc}$ (°C) | Peak $T_m$ (°C) | $\Delta H_m$ (J/g) | $w_{c,hPN}$
<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>hPHFAN-41</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hP(N-HFAN)-17</td>
<td>48</td>
<td>108</td>
<td>132</td>
<td>29.4</td>
<td>0.79</td>
</tr>
<tr>
<td>hP(N-HFAN)-25</td>
<td>49</td>
<td>134</td>
<td></td>
<td>20.8</td>
<td>0.57</td>
</tr>
<tr>
<td>hP(N-HFAN)-43</td>
<td>53</td>
<td>126</td>
<td>142</td>
<td>21.8</td>
<td>0.56</td>
</tr>
<tr>
<td>hP(N-HFAN)-69</td>
<td>47</td>
<td>117</td>
<td>141</td>
<td>21.8</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$\Delta H_m$ calculated from the melting enthalpy ($\Delta H_m$) using $\Delta H_{m,100} = 86$ J/g.\(^{21}\)

Given the preliminary evidence for microphase separation provided by DSC and the nearly symmetric (volumetric) compositions (Table 7.4), the melt morphology is expected to be lamellar. The microdomain morphology was studied in detail by 2D small-angle x-ray scattering (SAXS) on flow-aligned specimens. Each polymer was subjected to uniaxial planar extensional flow in the melt using a lubricated channel die and cooled to room temperature. The extensional flow field is used to align the otherwise isotropic lamellar microdomains in the melt.\(^{3,9,12,30-32}\) The extensional axis is labeled “flow direction” (FD), the compression axis is the “load direction” (LD), and the “constraint direction” (CD) is the neutral direction. Figure 7.4a–c shows the 2D SAXS patterns of hP(N-HFAN)-43 taken at room temperature with the beam aligned with each of the three principle axes. The CD pattern shows four structure factor peaks in integer ratios (though the even-order peaks are damped because the composition is nearly symmetric), confirming the lamellar morphology.
Figure 7.4. 2D SAXS patterns of hP(N-HFAN)-43 with the beam directed down CD (a), FD (b), and LD (c) at room temperature. Azimuthal traces obtained by integrating the primary peak \( q = 0.09-0.14 \text{ nm}^{-1} \) (d), arrows denote the position of the beamstop support. Illustration of the microdomain morphology after alignment (e).
The azimuthal traces of the primary peak show the degree of alignment in each of the three directions (Figure 7.4d). In the CD view, the scattered intensity is concentrated along LD, indicating that the microdomains are predominantly oriented with the lamellar normals (n) parallel to LD. The CD view also shows both the highest peak intensity and strongest alignment (I_max/I_min ≈ 100). In comparison, the FD view shows high scattered intensity which is only weakly concentrated along LD, and the LD view shows modest alignment along CD but much weaker intensity. These observations are consistent with the microdomain orientation depicted in Figure 7.4e. Orientations with a component of n along FD are strongly disfavored by the flow field and are thus essentially absent (there is no appreciable scattering along FD in either the CD or LD views). The strong scattering and alignment in the CD view indicate that the majority of the lamellae have n coincident with LD. A population of lamellae with n parallel to CD is also present, as evidenced by the comparatively poor degree of alignment in the FD view and the weak but clear scattering along CD in the LD view. These lamellae do not contribute to the scattering when the x-ray beam is along CD; hence the CD view is used extensively going forward.

If the hPN crystallites were aligned with the c-axis parallel to the microdomain interfaces, as observed for LPE crystals under confinement, the hPN crystal-amorphous scattering should appear in the SAXS patterns. The crystal-amorphous scattering would appear as broad scattering maxima orthogonal to the microdomain scattering, particularly in the LD view. However, no such scattering is observed; in fact, radial traces taken 90° from the microdomain peaks in all three views are featureless. This serves as an early indication that the hPN crystal orientation is not what is observed for LPE.
Figure 7.5 shows the azimuthally integrated 1D SAXS patterns of all four diblock copolymers acquired in the CD view. In the melt (at 160°C), the patterns of each of the four polymers show several (as many as 5) higher-order peaks in integer ratios, confirming that all four polymers adopt lamellar morphologies in the melt. The large number of reflections and the observation that the lowest molecular weight diblock, hP(N-HFAN)-17, remained ordered to at least 200 °C, indicate that the diblocks are strongly segregated. The domain spacings calculated from the melt patterns are plotted versus $M_{LS}$ in Figure 7.6. Despite the somewhat broad distributions of the two lower molecular weight polymers, the strong segregation scaling law $^{33} d \sim N^{2/3}$ (where $N$ is proportional to $M$ for constant composition) describes the data quite well.
Figure 7.5. Radially integrated 1D SAXS patterns of the hP(N-HFAN) diblocks taken with the x-ray beam along CD in the melt at 160 °C (a) and after crystallizing by cooling to 100 °C at ≈1 °C/min (b). The expected positions of the lamellar structure factor peaks (at $q/q^* = 1, 2, 3, 4, 5,$ and 6 based on the measured $q^*$) are indicated by triangles.
Figure 7.6. Lamellar domain spacings ($d$) obtained by SAXS 160 °C plotted against the number average molecular weight determined by light scattering. The solid line represents the fit to the data $d = 3.87M_{LS}^{2/3}$, where $d$ [=] nm and $M_{LS}$ [=] kg/mol. Using $M_{n,r}$ in place of $M_{LS}$ yields $d = 4.22M_{n,r}^{2/3}$.

In strongly segregated block copolymers, the centers of the microdomains are essentially pure; however, there exists a finite region of segmental mixing at the domain interface. The breadth of this interfacial mixing region can be used to assess the degree of segregation between the blocks. The electron density profile of the melt structure can be modeled as a simple square wave with step height $\Delta \rho_e = |\rho_{e,hPHFAN} - \rho_{e,hPN}|$ convolved with a Gaussian which imparts a smoothly varying electron density profile (mixing region) across the interface, approximated by a linear gradient with width $t_i$. The finite interfacial breadth serves to damp the structure factor peaks in the SAXS pattern according to:
\[ I_m \sim m^{-4} \Delta \rho_c^2 \sin^2 (m \pi \phi_A) e^{-km^2} \]  \[7.1\]

where \( m \) is the order of reflection (i.e., \( m = q/q^* = 1, 2, 3, \) etc.) and \( k = 2\pi(t/d)^2 \) is the damping factor.\(^{39}\) The intensity of the even-order peaks is a sensitive function of the A component volume fraction (\( \phi_A \)) near \( \phi_A \approx 0.5 \); however, the identity of A (i.e., whether A is hPN or hPHFAN) cannot be determined from the SAXS data alone due to the loss of phase information. Based on the volume fractions computed from the weight fractions and specific volume correlations\(^{27,28}\) \( \phi_A \geq 0.5 \) is presumed to be \( \phi_{hPN} \). If at least three SAXS peaks are present, \( \phi_A \) and \( k \) can be calculated from the integrated peak intensities \( (I_m) \) of the higher order peaks normalized by that of the primary peak \( (I_2/I_1, I_3/I_1, \) etc.).

The results of the model fits, along with the melt \( d \) spacings, are shown in Table 7.4. The well-resolved higher-order peaks in the SAXS patterns of hP(N-HFAN)-17 and -43 allowed \( \phi_A \) and \( k \) to be fit simultaneously. Though equation \([7.1]\) is only strictly true for SAXS patterns acquired from isotropic specimens, the values of \( \phi_A \) are in good agreement with the values determined using specific volume correlations,\(^{27,28}\) validating the approach. The damping factor for hP(N-HFAN)-25 was calculated from \( I_2/I_1 \) assuming \( \phi_A = \phi_{hPN} \). The primary peak of hP(N-HFAN)-69 was partially obstructed by the beamstop, precluding an accurate calculation of \( I_1 \). The calculated interfacial regions are quite narrow, ranging from 3–4 nm, and constitute only about 10% of the domain period \( (t/d \approx 0.1) \). For comparison, two systems (block-random copolymers of mid-vinyl polyisoprene (hI) and polystyrene\(^{40}\) at 23 °C and diblock copolymers of polystyrene and poly(methyl methacrylate)\(^{41,42}\) at 105 °C) with interaction energy densities \( X \approx 1 \) MPa had \( t_i \approx 4.5–6 \) nm. The somewhat narrower apparent interfacial breadth in the hP(N-HFAN) diblocks is consistent with a larger \( X \) between hPN and hPHFAN.\(^{34}\) Equation \([7.1]\) under predicts the intensity of the even-order peaks in the solid state (Figure 7.5b) by over two...
orders of magnitude for hP(N-HFAN)-17 and -25, even for \( k = 0 \). This indicates that the simple
two-phase lamellar electron density profile does not accurately represent the morphology. In
particular the electron density of the semicrystalline hPN domains cannot be represented simply
as the average between the crystalline and amorphous hPN, consistent with the observation that
the crystals do appear to stack parallel to the interfaces.

Table 7.4. Domain Spacings, Volume Fractions, and Interfacial Breadths for
hP(N-HFAN) Diblock Copolymers at 160 °C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( d ) (nm)</th>
<th>( \phi_{hPN} )</th>
<th>( I_2/I_1 \times 10^3 )</th>
<th>( I_3/I_1 \times 10^3 )</th>
<th>( I_5/I_1 \times 10^3 )</th>
<th>( \phi_A )</th>
<th>( k )</th>
<th>( t_i/d )</th>
<th>( t_i ) (nm)</th>
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</thead>
<tbody>
<tr>
<td>hP(N-HFAN)-17</td>
<td>28.4</td>
<td>0.518</td>
<td>4.46</td>
<td>5.45</td>
<td>0.548</td>
<td>0.0786</td>
<td>0.112</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>hP(N-HFAN)-25</td>
<td>37.3</td>
<td>0.513</td>
<td>2.61</td>
<td></td>
<td></td>
<td>0.0703\textsuperscript{b}</td>
<td>0.104</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>hP(N-HFAN)-43</td>
<td>49.8</td>
<td>0.544</td>
<td>2.88</td>
<td>8.21</td>
<td>0.613</td>
<td>0.536</td>
<td>0.0373</td>
<td>0.077</td>
<td>3.8</td>
</tr>
<tr>
<td>hP(N-HFAN)-69</td>
<td>71.5</td>
<td>0.541</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated using \( w_{hPN} \) in Table 7.2 and density correlations,\textsuperscript{27,28} \textsuperscript{b}computed using \( \phi_{hPN} \).
7.3 Crystal Confinement

Crystallization within spherical or cylindrical domains is typically characterized as confined (or templated) if crystallization does not bring about substantive changes in the morphology\textsuperscript{12} (often assessed by the position of the primary SAXS peak). In comparison, the criteria for confinement are less well established for soft lamellar microdomains, where crystallization is restricted in one dimension only and the microdomains are interconnected and flexible. One way to define confinement is in relation to the other extreme, where the melt morphology is destroyed and crystallization dictates the solid-state morphology. This level of structural rearrangement requires crystallizable chains to diffuse through the amorphous phase to add to the growing crystallites which propagate isotropically. Thus, confined (or templated) crystallization is defined as the situation where the crystallizable chains are prevented from diffusing into the amorphous domains and the crystallites are forced to grow within their corresponding microdomains. This may seem obvious, but it is important to realize that crystallization can distort the structure even when this criterion is met. Therefore, simply tracking the primary peak position by SAXS may be insufficient to determine whether crystallization is confined.

To determine whether the segregation strength is sufficient to prevent breakout of the hPN crystallites, flow aligned specimens of each diblock were repeatedly melted and recrystallized while monitoring the microdomain orientation by 2D SAXS. If breakout were to occur, crystallization would randomize the microdomain orientation and the patterns would become isotropic. The 2D SAXS patterns of the CD view of hP(N-HFAN)-43 over the course of three recrystallization cycles are shown in Figure 7.7. The patterns reveal a high degree of orientation throughout, indicating that the crystallization does not destroy the melt morphology.
Azimuthal traces of the primary peak (Figure 7.8) show minimal loss of orientation over the course of three cycles. The orientation of hP(N-HFAN)-25 also drops only modestly after five cycles. Crystallization causes a somewhat more pronounced azimuthal broadening in hP(N-HFAN)-17 after the first cycle; however, the incremental loss of orientation on subsequent cycles indicates that the melt microstructure is not destroyed during crystallization and the crystals are largely confined. Patterns of hP(N-HFAN)-69 exhibited poor initial alignment, but showed no evidence of breakout as expected from the results of the lower molecular weight polymers.

Figure 7.7. 2D SAXS patterns of hP(N-HFAN)-43 in the CD view after repeatedly melting by heating to 160 °C and recrystallizing by slowly (∼1 °C/min) cooling to 100 °C and holding for 30 min.
Figure 7.8. Azimuthal traces of the primary SAXS peak of hP(N-HFAN)-17 (a), hP(N-HFAN)-25 (b), and hP(N-HFAN)-43 (c) after flow aligning (cycle 0) and repeatedly melting and recrystallizing by cooling to 100 °C (at ≈1 °C/min). Azimuthal traces of hP(N-HFAN)-43 correspond to the patterns in Figure 7.7. All patterns were acquired at 100 °C except cycle 0 in panel (c) which was collected at room temperature.
The lamellar morphology is retained in the solid state, as evidenced by the higher-order peaks in integer ratios in the 1D traces in Figure 7.5b, however, the characteristic lamellar period dilates substantially upon crystallization. Figure 7.9 shows the $d$-spacing in the melt and solid states as a function of the number of recrystallization cycles. In hP(N-HFAN)-43 and -69, $d$ is 18% larger in the solid state than in the melt. The largest change is observed in hP(N-HFAN)-17 where crystallization increases the $d$-spacing by >30%. These large changes cannot be explained by the 5–6% reduction in density associated with hPN crystallization, from which one would predict a smaller $d$ in the semicrystalline state. Rather, the growing crystallites must expand the hPN domains in the direction normal to the interfaces. Since the total density decreases, this expansion may be explained by a large contraction of the grains in the orthogonal directions, a reduction in the number of lamellae per grain, or buckling of the lamellae. Though the solid-state $d$-spacing increases slightly following the first recrystallization cycle, there is little change in the $d$-spacing in the melt or solid states on subsequent cycles, indicating that this process is highly reversible. In addition, the azimuthal traces indicate that the crystals do not break out, meaning that diffusion of the hPN blocks through the hPHFAN domains is suppressed. Thus, the facile destruction and creation of lamellae on crystallization and melting seems unlikely. The presence of buckling would be marked by a transition from a two-spot SAXS pattern to a four-spot pattern, which is not observed.
Figure 7.9. Lamellar domain spacings ($d$) obtained by SAXS in the solid state at 100 °C (filled symbols) and in the melt at 160 °C (open symbols) taken in the CD view as a function of the number of melting/recrystallization cycles. Cycle 0 corresponds to the specimen after flow alignment; the $d$-spacing of hP(N-HFAN)-17 in cycle 0 was measured at room temperature.

7.4 Crystal Orientation and Thickening

The orientation of the hPN crystallites with respect to the lamellar microdomain structure was assessed using 2D wide-angle x-ray scattering (WAXS) on flow aligned specimens. Specimens were cut from material which had been crystallized in the channel die (at a cooling rate of 1–5 °C/min). Figure 7.10 shows 2D WAXS patterns of hP(N-HFAN)-43 and hP(N-HFAN)-17 in the CD view. Two strong reflections, the (020) and (110) peaks, belonging to the monoclinic unit cell of hPN homopolymer$^{21}$ at room temperature are observed. Azimuthal traces
of these two peaks were used to determine the crystal orientation. Whereas the azimuthal traces of the (020) reflections show sharp peaks centered on the equator, the azimuthal traces of the (110) peaks show complex splitting (Figure 7.10). A detailed description of the split angle calculations is presented in Appendix B. In short, the split angles ($\psi$) of the (020) and (110) peaks are consistent with the $b$-axis lying parallel to the microdomain interfaces with the crystal stems ($c$-axis) tilted with respect to $n$ about the $b$-axis with free rotation of the crystallites about $n$ (as depicted in Figure 7.11). This assignment is consistent with the conclusions from the SAXS data above, which indicate that the $c$-axis is not parallel to the domain interfaces. The observed multiple splitting of the (110) peaks may arise from misaligned lamellae which are rotated about FD, as evidenced by the 2D SAXS patterns of hP(N-HFAN)-43 in the FD and LD views (Figure 7.4). Another possibility is that two populations of crystallites with different tilts coexist. Taking the sharp reflections in the CD view of hP(N-HFAN)-17 as indicative of the primary crystal orientation yields a $c$-axis tilt of $\approx$21° (with respect to $n$). The split angle of the (110) peaks of hP(N-HFAN)-25, and hence the $c$-axis tilt, is the same as that of hP(N-HFAN)-17. Assuming that the complex splitting pattern arises from a fixed crystal orientation and rotation of the lamellae about FD, the $c$-axis tilt of hP(N-HFAN)-43 is found to be $\approx$40°. This orientation places both the $a$ and $b$ axes in the CD-FD plane. The degree of alignment in hP(N-HFAN)-69 is insufficient to determine the crystal orientation.
Figure 7.10. 2D WAXS patterns in the CD view of hP(N-HFAN)-43 (a) and hP(N-HFAN)-17 (d) and azimuthal traces of the (020) peaks (b and e) and the (110) peaks (c and f). The azimuthal angle is defined in the counterclockwise direction from the 3 o’clock position (0°). The meridian (azimuth = 90° and 270°) corresponds to LD in both the CD and FD views. In the LD view the meridian is CD.
Figure 7.11. Schematic representation of the hPN crystal orientation under lamellar confinement. Blue lines represent an hPN crystallite, red planes indicate the microdomain interfaces, and $\lambda$ is the tilt angle.

The crystallite orientation determined from the WAXS patterns is consistent with the lack of detectable scattering from the crystalline-amorphous hPN repeat distance in any of the SAXS patterns. As a consequence, the crystal thickness ($t_c$) could not be measured directly by SAXS. Instead, crystal thickening was studied by measuring the melting point as a function of isothermal annealing temperature ($T_a$) and time ($\tau$) using DSC. Specimens were crystallized by quenching from the melt to room temperature and then annealed by rapidly heating and holding at temperature $T_{cc} < T_a < T_m$. Homopolymer hPN thickens rapidly under these conditions. The specimens were then rapidly cooled to ca. 100 °C and immediately melted at 10 °C/min to capture the majority of the melting endotherm. To determine the optimal annealing temperature, where the crystals formed during the initial quench thicken rapidly but do not melt when heated to $T_a$, the $T_m$ and $\Delta H_m$ were measured as function of $T_a$ for $\tau = 100$ min. The peak $T_m$ values are plotted versus $T_a$ in Figure 7.12. The region labeled “melting and recrystallization” was
characterized by a drop in $\Delta H_m$ or in some cases bimodal melting endotherms, indicating that some of the crystallites formed during the quench had melted during annealing and recrystallized when the specimens were cooled to 100 °C. The optimal $T_a$ was chosen for each polymer to maximize $T_m$ while avoiding melting and recrystallization; $T_a = 126$ °C for hP(N-HFAN)-17, 128 °C for hP(N-HFAN)-25, and 134 °C for hP(N-HFAN)-43 and -69.

\[ \text{Figure 7.12. Peak melting point (} T_m \text{) after annealing at } T_a \text{ for 100 min.} \]
Having chosen \( T_a \) for each polymer, \( T_m \) was measured as a function of annealing time (Figure 7.13a). The melting point (in absolute units) is related to the crystal thickness through the Gibbs-Thomson equation, which accounts for the melting point depression associated with the interfaces between the crystalline and amorphous phases. Equation [7.2] is the Gibbs-Thomson equation written for disk-like crystallites of thickness \( t_c \) and radius \( R_c \), where \( \Delta H_{m,100} \) is the melting enthalpy of 100% crystalline hPN, \( \rho_c \) is the density of the crystalline phase at \( T_m \), \( \sigma_f \) is the fold surface energy, and \( \sigma_s \) is surface energy of the lateral surfaces.

\[
1 - \frac{T_m}{T_m^0} = \frac{2}{\Delta H_{m,100}\rho_c} \left( \frac{\sigma_f}{t_c} + \frac{\sigma_s}{R_c} \right) \quad [7.2]
\]

If the crystal orientation determined by WAXS is correct, the crystallites can grow unimpeded in plane of the microdomains, resulting in \( R_c \gg t_c \); in this scenario the contribution of the lateral surfaces is negligible and equation [7.2] can be simplified and rearranged to equation [7.3] (equivalent to equation [2.2]).

\[
t_c = \frac{2\sigma_f}{\Delta H_{m,100}\rho_c} \left( 1 - \frac{T_m}{T_m^0} \right)^{-1} \quad [7.3]
\]

Crystal thicknesses were calculated for the confined diblock copolymers using equation [7.3] with \( T_m^0 = 153 \, ^\circ\text{C} \), \( \Delta H_{m,100} = 83 \, \text{J/g} \), and \( \sigma_f = 0.031 \, \text{J/m}^2 \), which have been measured for homopolymer hPN.\(^{43}\) These material constants correspond to the rotationally disordered crystal structure which is observed prior to melting.
Figure 7.13. Peak $T_m$ as a function of annealing time ($\tau$) (a) and the crystal thicknesses ($t_c$) calculated therefrom using equation [7.3] (b). Horizontal lines represent the hPN domain layer thickness (given by $\phi_{hPNd}$) calculated at 100 °C.
As can be seen from Figure 7.13b, the two lower molecular weight polymers undergo only modest crystal thickening, and the maximum crystal thickness calculated using equation [7.3] is essentially equal to the thickness of the hPN domains ($\phi_{hPN}d$ measured by SAXS at 100 °C on the last melting/recrystallization cycle, Figure 7.9). The two higher molecular weight polymers undergo substantial crystal thickening. The calculated crystal thickness of hP(N-HFAN)-43 exceeds $\phi_{hPN}d$ even at the shortest annealing time and appears to plateau near 50 nm, indicating that the crystal thickness is limited by confinement. hP(N-HFAN)-69 shows apparent crystal thicknesses which exceed the maximum allowable crystal thickness at long annealing times, but a plateau is not observed.

If the crystal orientation shown in Figure 7.11 is correct, a layer of amorphous hPN should reside between the crystal fold surfaces and the microdomain interfaces. Thus, the maximum possible crystal thickness is given by $t_{c,max} = \phi_c \phi_{hPN}d$. Given that at the longest annealing time $\phi_c \approx 0.75$ for all but hP(N-HFAN)-25 (where $\phi_c \approx 0.60$), it is clear that the measured $t_c > t_{c,max}$ for all four polymers. This does not arise from the simplifying assumption of large lateral extent; in fact, the full Gibbs-Thomson expression (equation [7.2]) would yield even larger values of $t_c$ for a given measured $T_m$. One aspect of the application of equation [7.3] that can be called into question is the value of $\sigma_f$. Given the tilt of the crystal stems, the crystallographic indices of the fold surfaces in the confined crystals differ from that of the homopolymer. In addition, the fold surface energy is likely altered by the adjacent microdomain interfaces. Thus, the true value of $\sigma_f$ in the block copolymer likely differs from the measured value for the homopolymer. To bring the calculated crystal thickness into agreement with $t_{c,max}$ for hP(N-HFAN)-17, the fold surface energy would have to be reduced by 20%. A reduction in $\sigma_f$ of 40% would be required to rectify the discrepancy for hP(N-HFAN)-25, which is thought to
have the same crystal orientation, indicating that changes in the fold surface energy may not be the only explanation. The fold surface energy of the crystallites in hP(N-HFAN)-43 would have to be reduced by 55% to make the limiting measured $t_c$ equal to $t_{c,\text{max}}$.

### 7.5 Conclusions

Crystalline-amorphous diblock copolymers containing hPN have been prepared and characterized. All four diblocks studied are found to exhibit strongly segregated lamellar morphologies in the melt. Upon crystallization the morphology is again lamellar; however, the characteristic periodicity increases substantially. In spite of the change in $d$-spacing, flow aligned specimens show minimal loss of orientation upon repeated melting and recrystallization. These observations indicate that the rubbery amorphous domains prevent the crystallites from breaking out while also accommodating dilation of the domain structure. The crystal orientation deduced from the WAXS patterns places the $b$-axis in the plane of the microdomain interfaces, while the $c$-axis is tilted with respect to the lamellar normals, resembling the orientation of EO crystallites at moderate undercoolings. The tilt angle apparently increases with increasing molecular weight. Crystal thickening was studied by measuring the peak melting points as a function of annealing time by differential scanning calorimetry; crystal thicknesses were calculated using the Gibbs-Thomson equation. The two lower molecular weight polymers undergo modest crystal thickening and the apparent calculated crystal thicknesses are equal to the hPN domain thickness. In the case of the two higher molecular weight polymers the apparent $t_c$ exceeds the maximum possible value, given the orientation of the crystallites. This discrepancy may arise from changes in the fold surface energy, or may indicate that the assigned
crystallite orientation is incorrect. Direct measures of the crystallite orientation and thickness, such as by electron microscopy, are required to definitively answer these questions.
7.6 References


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28. See Appendix A


Chapter 8

Structure and Thermal Properties of Hydrogenated Tactic Polynorbornenes

Tacticity describes the relative placement of chiral centers down the backbone of a polymer. Three basic arrangements are commonly encountered: atactic (a), isotactic (i), and syndiotactic (s). If the chains were extended, the substituents on the atactic chain would fall randomly on either side of the chain, while the substituents on the isotactic chain would reside exclusively on one side of the chain and the substituents on the syndiotactic chain would strictly alternate sides. The degree of tacticity is characterized by the ratio of meso to racemo diads; isotactic polymers comprise exclusively meso diads, whereas syndiotactic polymers are entirely racemo. The previous chapter made use of the uncommon feature that hydrogenated atactic ring-opened polynorbornene (ahPN) can crystallize. In most cases, atactic polymers are amorphous because the random placement of substituents does not allow the segments to fit into a regular lattice. In polynorbornene tacticity arises from the nonplanar cyclopentylene rings enchained in the backbone (Figure 8.1). Hydrogenation eliminates cis/trans isomerism but the tacticity remains. Evidently the difference between the two cyclopentylene configurations is subtle enough that both hydrogenated units can pack into a common lattice.\(^1\) This same subtlety makes controlling the tacticity during polymerization challenging. Stereospecific ring-opening metathesis polymerization (ROMP) of norbornene has been achieved using initiators developed
by Schrock et al.\textsuperscript{2} and Hayano et al.\textsuperscript{3,4} Hydrogenated ROMP polynorbornene thus affords the unique opportunity to study the effect of all three basic tacticities on the crystal structure and properties.

\textbf{Figure 8.1.} Illustration of \textit{isotactic} (top) and \textit{syndiotactic} (bottom) polynorbornene before (left) and after (right) hydrogenation. Two adjacent repeat units with the same configuration constitute a \textit{meso} (\textit{m}) dyad, while adjacent repeat units with opposite configurations are a \textit{racemo} (\textit{r}) dyad.
8.1 Preparation of Hydrogenated Tactic Polynorbornenes

* cis,isotactic and cis,syndiotactic* polynorbornene (PN) were synthesized and generously provided by Benjamin Autenrieth of the Schrock group at the Massachusetts Institute of Technology. The synthetic route has been described in detail in one of their recent publications."\(^2\) The initiators used are shown in Figure 8.2. The *isotactic* polymer is prepared using initiator 2; the chiral biphenolate ligand forces the monomer to approach the active site from the same side during each addition (called enantiomorphic site control). Initiator 3 is used to prepare *syndiotactic* PN; after each monomer insertion the configuration of the aryloxide and pyrrolide ligands switches such that each monomer must approach the active site from the opposite side as the previous monomer. Polymerizations initiated by 2 or 3 are nonliving and complete monomer conversion is achieved within minutes. In some cases an α-olefin such as 1-hexene was used as a chain transfer agent to control the molecular weight. The tacticity of the unsaturated PNs was confirmed by the Schrock group using "\(^{13}\)C NMR."\(^2,5\) The stereochemistry of *cis,isotactic* and *cis,syndiotactic* PN render both polymers semicrystalline with melting points of 56 °C and 61 °C, respectively, but this was not explored in further detail due to the susceptibility of the backbone unsaturation to degradation. The ahPN homopolymers used for comparison throughout this chapter was prepared by living ROMP using initiator 1 and hydrogenated with Pd/CaCO\(_3\) and were reported by Lee and Register"\(^1\) or Showak et al."\(^6\)
Figure 8.2. Ring-opening metathesis polymerization initiators for the preparation of atactic (1), cis,isotactic (2), and cis,syndiotactic (3) polynorbornene.

The molecular weights and distributions of the unsaturated polymers were characterized by gel permeation chromatography (GPC) in THF using the system described in Chapter 3. The traces are shown in Figure 8.3, and the derived quantities can be found in Table 8.1. Small peaks appearing at the end of the chromatograms are attributed to ROMP initiator residues and were excluded from the molecular weight and distribution analysis. The weight average molecular weights ($M_{\text{w}}$) were estimated using the specific refractive index increment measured for aPN synthesized with initiator 1 ($dn/dc = 0.1549$ mL/g). The $dn/dc$ depends principally on the identity of the functional groups and not the stereochemistry. For example the $dn/dc$ for isotactic and atactic poly(methyl methacrylate) (in acetone at 25 °C and $\lambda = 346$ μm or 546 μm) are found to be equal, and the $dn/dc$ of isotactic and atactic polypropylene (in 1-chloronaphthalene at 140 °C and $\lambda = 546$ μm) differ by less than 4%, likely within the uncertainty of the measurement.⁷
Table 8.1. Molecular Characteristics of Unsaturated Tactic Polynorbornenes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{L5}$ (kg/mol)</th>
<th>$M_{w,PS}$ a (kg/mol)</th>
<th>$\bar{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis,iso PN-A</td>
<td>98.2</td>
<td>83.7</td>
<td>2.06</td>
</tr>
<tr>
<td>cis,iso PN-B</td>
<td>89.5</td>
<td>74.3</td>
<td>2.26</td>
</tr>
<tr>
<td>cis,syndio PN</td>
<td>64.0</td>
<td>68.0</td>
<td>1.72</td>
</tr>
</tbody>
</table>

aPolystyrene equivalent molecular weight.

Figure 8.3. Gel permeation chromatography traces of the cis,isotatic PN (a) and cis,syndiotactic PN (b) unsaturated precursors. Traces are plotted on a common vertical scale to facilitate comparison. The peaks eluting at 18–19 min presumably correspond to ROMP initiator residues.
The tactic PNs were saturated using either the supported palladium catalyst (Pd/CaCO₃) in cyclohexane or the organometallic ruthenium complex Ru(CO)ClH(PPh₃)₃ in xylenes as described in previous chapters. The reaction progress was monitored by ¹H NMR spectroscopy at 120 °C in 1,1,2,2-tetrachloroethane-d₂; all of the polymers were fully soluble under these conditions. The reaction conditions and fractional conversions are listed in Table 8.2. Special care was taken to maximize the degree of saturation; hence, the reaction temperatures and times in Table 8.2 are higher and longer than in previous chapters. To confirm that no adverse side reactions occurred during hydrogenation, the molecular weight distribution of ihPN-Pd was characterized by high temperature GPC using a Viscotek 350A HT-GPC system operating at 150 °C with 1,2-dichlorobenzene with 500 ppm butylated hydroxytoluene. The author is grateful to Maggie Tiedemann of the Carrow group at Princeton for her help with these measurements. Samples were dissolved in either the mobile phase or decalin stabilized with 500 ppm galvinoxyl. The apparently small dn/dc of hPN in 1,2-dichlorobenzene (at 150 °C and λ = 670 nm) precluded analysis by refractive index or light scattering. Therefore, the viscometry data was used to compare the molecular weight distributions prior to and following hydrogenation. Figure 8.4 clearly shows that the molecular weight distribution was not altered by hydrogenation. The tacticity was checked by ¹³C NMR spectroscopy after hydrogenation; each peak remains sharp and narrow with no evidence of racemization (Figure 8.5).²⁴⁻⁵
### Table 8.2. Hydrogenation Conditions and Fractional Saturation for Tactic Polynorbornenes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Precursor</th>
<th>Hydrogenation Catalyst/Conditions</th>
<th>Fractional Saturation$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$hPN-Pd</td>
<td>cis,iso PN-A</td>
<td>Pd/CaCO$_3$, cyclohexane, 120–160 °C, 3.2 days</td>
<td>0.998</td>
</tr>
<tr>
<td>$i$hPN-Ru</td>
<td>cis,iso PN-B</td>
<td>Ru(CO)ClH(PPh$_3$)$_3$, xylene, 140–160 °C, 9.4 days</td>
<td>0.999</td>
</tr>
<tr>
<td>$s$hPN-Ru</td>
<td>cis,syndio PN</td>
<td>Ru(CO)ClH(PPh$_3$)$_3$, xylene, 140 °C, 6.6 days$^a$</td>
<td>0.995</td>
</tr>
</tbody>
</table>

$^a$Additional charges of Ru(CO)ClH(PPh$_3$)$_3$ and Pd/CaCO$_3$ were unsuccessful in increasing the fractional saturation. $^b$Calculated by $^1$H NMR at 120 °C in 1,1,2,2-tetrachloroethane-d$_2$.

---

**Figure 8.4.** High temperature GPC traces of cis,iso PN-A and $i$hPN-Pd showing no evidence of adverse side reactions during hydrogenation.
Figure 8.5. $^{13}$C NMR spectra of $i$hPN-Pd (a) and $s$hPN-Ru (b) acquired at 120 °C in 1,1,2,2-tetrachloroethane-$d_2$. 
8.2 Thermal Properties

The thermal properties of the tactic hPNs were investigated using differential scanning calorimetry (DSC). Figure 8.6 shows the heating and cooling traces collected with a scan rate of 10 °C/min; the peak melting points ($T_m$) and melting enthalpies ($\Delta H_m$) are shown in Table 8.3. Interestingly, the melting points of shPN and ihPN, crystallized on dynamic cooling, bracket that of ahPN. The melting point of ihPN is some 20 °C higher than that of ahPN, whereas shPN has a lower $T_m$ than ahPN by approximately 15 °C, despite its stereoregularity. The small endotherm observed in the melting trace of ihPN-Pd near 133 °C is reminiscent of the crystal-crystal transition in ahPN;\textsuperscript{1,8} this point will be revisited subsequently. Hayano and Nakama prepared fully isotactic hPN ($M_n = 23.4$ kg/mol, $D = 5.2$, and $m:r = 100:0$) and highly syndiotactic hPN ($M_n = 10.8$ kg/mol, $D = 1.7$, $m:r = 8:92$, and $mm:mm\text{r}:mm\text{r}:rr = 5:10:85$) using Mo or W-based binary catalyst systems.\textsuperscript{4} DSC measurements conducted on dynamically crystallized specimens with a scan rate of 10 °C/min yielded $T_m = 178$ °C and $\Delta H_m = 55$ J/g for the isotactic polymer, and $T_m = 132$ °C and $\Delta H_m = 62$ J/g for the highly syndiotactic polymer. The peak $T_m$ values reported by Hayano and Nakama are systematically higher than those reported here, which may stem from differences in the molecular weight and distribution or the tacticity; however, the trend of increasing $T_m$ with increasing meso content (isotacticity) is consistent. Hayano and Nakama also reported larger $\Delta H_m$ values (it is important to note that these values are sensitive to the choice of the integration region), but the trend of decreasing $\Delta H_m$ with increasing meso content is again consistent with the present work. The glass transition temperatures of both ihPN and shPN were estimated on heating to be $\approx8$ °C (Figure 8.7), similar to $T_g = 4$ °C reported for ahPN.\textsuperscript{9}
Figure 8.6. Differential scanning calorimetry traces of the tactic polynorbornenes and ahPN reported by Showak et al.\textsuperscript{6} on heating (a) and cooling (b) at 10 °C/min.
Figure 8.7. Expanded view of the glass transition region of the differential scanning calorimetry traces of the tactic polynorbornenes on heating.

Table 8.3. Thermal Properties, WAXS Crystallinity, and Density of Tactic hPNs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Peak $T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$w_{c,WAXS}$</th>
<th>$\rho_{23}^a$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{h}$hPN-Pd</td>
<td>7</td>
<td>164</td>
<td>40.4</td>
<td>0.46</td>
<td>0.9956</td>
</tr>
<tr>
<td>$\tilde{h}$hPN-Ru</td>
<td>9</td>
<td>166</td>
<td>37.9</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>shPN-Ru</td>
<td>8</td>
<td>128</td>
<td>47.8</td>
<td>0.56</td>
<td>1.0113</td>
</tr>
<tr>
<td>$\sigma$hPN</td>
<td>4$^9$</td>
<td>140$^6$</td>
<td>66$^6$</td>
<td>0.64$^6$</td>
<td>0.9954$^1$</td>
</tr>
</tbody>
</table>

$^a$Mass density measured by William Jiao using a density gradient column at 23 °C.

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The melting points of \( \text{iPN-Ru} \) and \( \text{sPN-Ru} \) were further investigated by isothermally crystallizing and then melting specimens in the DSC. The measured peak melting points are plotted versus the crystallization temperature \( (T_c) \) in Figure 8.8. When isothermally crystallized at \( T_c \leq 154 \) °C the melting traces of \( \text{iPN-Ru} \) showed a single maximum. A small shoulder on the high-temperature edge of the melting endotherm was observed for \( T_c = 155 \) and 156 °C; a well-resolved second melting peak with \( T_{m,H} \approx 190 \) °C was observed for \( 157 \) °C \( \leq T_c \leq 161 \) °C. The lower-temperature peak \( (T_{m,L}) \) persists, and \( T_{m,L} \) continues to increase with increasing \( T_c \). The ratio of the melting enthalpies for the two peaks is \( \Delta H_{m,L}/\Delta H_{m,H} \approx 2 \). The bimodal melting is indicative of two distinct crystal structures, though it is unclear whether the high-temperature polymorph evolves by nucleation and growth of uncrystallized material or from a partial polymorphic transition. For comparison, \( \text{aPN} \) exhibits a complete polymorphic transition which is characterized by a small endotherm which precedes melting on heating or follows crystallization on cooling (Figure 8.6).

A linear Hoffman-Weeks extrapolation\(^1\) of \( T_{m,L} \) gives an estimate of the equilibrium melting point for the \( \text{iPN} \) of \( T_{m,0} \approx 195 \) °C. The evolution of the high-temperature endotherm adds uncertainty to this estimate. A more accurate value of \( T_{m,0} \) for the lower-melting polymorph could be obtained from Gibbs-Thomson analysis\(^6\) on specimens crystallized at \( T_c \leq 154 \) °C. The melting traces of \( \text{sPN-Ru} \) show no evidence of polymorphism over the range of \( T_c \) investigated. A linear Hoffman-Weeks extrapolation for \( \text{sPN} \) yields \( T_{m,0} \approx 143 \) °C. These estimates of \( T_{m,0} \) again bracket \( T_{m,0} = 153 \) °C determined for \( \text{aPN} \) by a Gibbs-Thomson analysis.\(^6\)
Figure 8.8. Hoffman-Weeks plots for \(i\)hPN-Ru (a), which shows two melting endotherms for \(157 \, ^\circ C \leq T_c \leq 161 \, ^\circ C\), and \(s\)hPN-Ru (b).
8.3 Structural Characterization

The crystal structure of the tactic hPNs was studied using wide-angle x-ray scattering (WAXS). 1D WAXS “powder” patterns were collected on 100–200 μm thick films prepared by melt pressing. The specimens were cooled on the bench top between hot aluminum plates (ca. 3 °C/min). The 1D WAXS patterns of \( ihPN-Ru \) and \( shPN-Ru \) are shown in Figure 8.9. The degree of crystallinity \( (w_{c,WAXS}) \) was estimated by fitting the amorphous scattering to the sum of three Gaussian functions. The resulting amorphous fits are shown as dashed lines in Figure 8.9, and the calculated crystallinities can be found in Table 8.3. By this metric, both \( ihPN \) and \( shPN \) are approximately 50% crystalline. The values calculated in this manner are highly sensitive to the amorphous fit; however, other common measures of crystallinity require additional parameters which are not known (i.e., the melting enthalpy of 100% crystalline polymer, \( \Delta H_{m,100} \), for DSC or the densities of the crystalline and amorphous phases for density measurements). Thus, comparisons across studies are less robust than comparisons within a single study. Nevertheless, higher values have been reported for \( ahPN \) \( (w_{c,WAXS} = 0.64–0.76) \).\(^{1,4,6}\) The results in Table 8.3 thus imply that the fully tactic polymers are somewhat less crystalline than \( ahPN \). For comparison, Hayano and Nakama reported \( w_{c,WAXS} = 0.50 \) for \( ihPN \), 0.67 for \( shPN \) \( (m:r = 8:92) \), and 0.66 for \( ahPN \) \( (m:r = 50:50) \). The results for \( ihPN \) and \( ahPN \) are consistent with those reported in Table 8.3; the discrepancy between \( shPN-Ru \) and the \( shPN \) reported by Hayano and Nakama likely stems from the difference in tacticity.
Figure 8.9. Wide angle x-ray scattering powder patterns of \textit{h}hPN-Ru (a) and \textit{s}hPN-Ru (b).

Dashed lines denote the amorphous scattering.
The crystal structures were studied in further detail using 2D WAXS on drawn fiber specimens. Fibers were prepared by melting a small quantity of material on a hot plate, grasping the melt with tweezers, and pulling. Drawing fibers aligns the chains in the drawing direction. As the fibers rapidly cool, crystallites nucleate and grow radially from the aligned chains, and hence exhibit rotational symmetry about the fiber axis.\textsuperscript{10-13} By convention the crystallographic axis coincident with the crystal stems (fiber axis) is assigned to the \(c\)-axis. Fibers were arranged in bundles to cover the x-ray beam. Fiber WAXS patterns of \(i\)hPN-Pd and \(s\)hPN-Pd are shown in Figure 8.10; the scattering angles \(2\theta_{hkl}\), calculated Bragg spacings \(d_{hkl}\), and split angles \(\psi\) are tabulated in Tables 8.4 and 8.5, respectively. The scattering angle was precisely calibrated by impregnating the fiber bundles with ground NaCl, which has a cubic unit cell with \(a = 5.6402\) Å.\textsuperscript{14} The sample-to-detector distance was calculated using the (111), (200), and (220) NaCl reflections, as described in detail elsewhere.\textsuperscript{15} The peak positions in the fiber patterns are in good agreement with the powder patterns (Figure 8.9), indicating that the fiber drawing process did not alter the crystal structure.
Figure 8.10. Wide-angle x-ray scattering fiber patterns of ihPN-Pd (top) and shPN-Ru (bottom) collected at room temperature.
Table 8.4. Scattering Angles, Bragg Spacings, Split Angles, and Relative Peak Intensities from Fiber Patterns of $ihPN$-$Pd$

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$2\theta_{hk\ell}$ (deg)</th>
<th>$d_{hk\ell}$ (Å)</th>
<th>$\psi^a$ (deg)</th>
<th>$I_{rel}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.8</td>
<td>5.99</td>
<td>180</td>
<td>4.1</td>
</tr>
<tr>
<td>B</td>
<td>17.1</td>
<td>5.20</td>
<td>119</td>
<td>5.6</td>
</tr>
<tr>
<td>C</td>
<td>18.3</td>
<td>4.85</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>D</td>
<td>20.1</td>
<td>4.43</td>
<td>0</td>
<td>19.4</td>
</tr>
<tr>
<td>E</td>
<td>21.2</td>
<td>4.18</td>
<td>0</td>
<td>26.9</td>
</tr>
<tr>
<td>F</td>
<td>26.9</td>
<td>3.32</td>
<td>67</td>
<td>0.67</td>
</tr>
<tr>
<td>G</td>
<td>30.6</td>
<td>2.92</td>
<td>58</td>
<td>0.54</td>
</tr>
<tr>
<td>H</td>
<td>33.3</td>
<td>2.69</td>
<td>180</td>
<td>0.62</td>
</tr>
<tr>
<td>I</td>
<td>36.2</td>
<td>2.48</td>
<td>0</td>
<td>3.1</td>
</tr>
<tr>
<td>J</td>
<td>40.7</td>
<td>2.22</td>
<td></td>
<td>8.4</td>
</tr>
</tbody>
</table>

$^a$azimuthal split angle across the equator, see Figure 8.12 and Appendix B for pictorial depictions, $^b$relative peak intensities normalized to 100 for the most intense peak.

Table 8.5. Scattering Angles, Bragg Spacings, Split Angles, and Relative Peak Intensities from Fiber Patterns of $shPN$-$Ru$

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$2\theta_{hk\ell}$ (deg)</th>
<th>$d_{hk\ell}$ (Å)</th>
<th>$\psi^a$ (deg)</th>
<th>$I_{rel}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.4</td>
<td>5.39</td>
<td>123</td>
<td>8.0</td>
</tr>
<tr>
<td>B</td>
<td>17.1</td>
<td>5.20</td>
<td>180</td>
<td>9.9</td>
</tr>
<tr>
<td>C</td>
<td>18.9</td>
<td>4.71</td>
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</tr>
<tr>
<td>D</td>
<td>19.4</td>
<td>4.58</td>
<td>0</td>
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<td>E</td>
<td>24.1</td>
<td>3.69</td>
<td>0</td>
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</tr>
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<td>0</td>
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<td>2.21</td>
<td></td>
<td>8.6</td>
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$^a$azimuthal split angle across the equator, see Figure 8.12 and Appendix B for pictorial depictions, $^b$relative peak intensities normalized to 100 for the most intense peak, $^c$reflections were resolved by collecting a pattern using bundle of only a few fibers.
The fiber pattern of \( \text{i}h\text{PN-Pd} \) shows a few strong peaks on the equator—i.e., the 0\(^{\text{th}}\) layer line, with Miller indices \((hk0)\). Several faint reflections can be seen on higher-order layer lines. The detector is a flat plate, so higher-order layer lines appear as hyperbolas centered on the meridian and spaced according to the \( c \)-axis Miller index \((l)\). The lack of strong higher-order peaks may indicate poor long-range order or a high degree of symmetry of the unit cell. Fiber patterns of \( \text{i}h\text{PN-Ru} \) closely resemble those of \( \text{i}h\text{PN-Pd} \), though the orientation is poorer. It can be seen from either the powder or fiber patterns that the crystal structure of \( \text{i}h\text{PN} \) is clearly distinct from \( \text{a}h\text{PN} \). The powder patterns of \( \text{a}h\text{PN}^{1,6} \) and \( \text{s}h\text{PN} \) are similar, as noted by Hayano and Nakama;\(^4\) however, the fiber patterns\(^1\) clearly illustrate that the crystal structures are distinct. Whereas the room temperature fiber pattern of \( \text{a}h\text{PN}^{1} \) shows clear reflections on the 1\(^{\text{st}}\), 2\(^{\text{nd}}\), 3\(^{\text{rd}}\), and 5\(^{\text{th}}\) layer lines, the \( \text{s}h\text{PN-Ru} \) reflections lie almost exclusively on the 0\(^{\text{th}}\) order layer line.

Fiber WAXS was also used to investigate the possibility of polymorphism in \( \text{i}h\text{PN} \). Unfortunately, the crystal structure corresponding to the high temperature melting endotherms observed in isothermally crystallized \( \text{i}h\text{PN-Ru} \) \((157 \, ^\circ\text{C} \leq T_c \leq 161 \, ^\circ\text{C}, \text{Figure 8.8})\) cannot be readily probed by fiber WAXS. The thermal history of the fibers is not well-controlled during drawing and the fibers cannot be melted and recrystallized without destroying the crystal orientation. Instead, temperature-dependent fiber WAXS was used to elucidate the potential crystal-crystal transition in \( \text{i}h\text{PN-Pd} \) near \( 133 \, ^\circ\text{C} \) (Figure 8.11). The fiber pattern of \( \text{i}h\text{PN-Pd} \) at \( 120 \, ^\circ\text{C} \) is nearly identical to that of the as-drawn fiber, indicating the crystal structure is unchanged. However, when the fibers were heated to \( 140 \, ^\circ\text{C} \), just above the small endotherm in the DSC heating trace, the WAXS patterns reveal a significant change. The most notable change is the emergence of four peaks split across the equator by \( \psi = 48^\circ \) (denoted \( \text{C}' \)). The intensity of the meridional reflections (denoted \( \text{A}' \)) is also significantly increased; the asymmetric intensity

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of the A’ reflections likely indicates that the fiber bundle is slightly tilted relative to the plane of the detector.\textsuperscript{10-13} The positions of the most intense reflections are not dramatically different from the as-drawn fiber patterns, consistent with the notion that solid-state phase transitions permit only a modest amount of structural rearrangement. Nonetheless, the changes in the fiber patterns clearly illustrate that \textit{i}hPN-Pd undergoes a polymorphic transition near 133 °C on heating.

The crystal structure exhibited by the as-drawn fibers was not recovered upon cooling to room temperature. Some radial broadening of the peaks is observed on cooling, but overall the transition is not readily reversible. Allowing the fibers to rest at room temperature for 15 days lead to increased radial and azimuthal broadening of the fiber WAXS peaks, but peaks observed at 140 °C persisted. The observation of a poorly reversible crystal-crystal transition was corroborated by DSC experiments. A specimen (which was crystallized on cooling at 10 °C/min) was heated to 140 °C and cooled below room temperature, to mimic the WAXS experiments, and then heated into the melt (all at 10 °C/min). The small endotherm corresponding to the crystal-crystal transition was observed in the first heating scan, but absent from the second. Thus the crystal-crystal transition attributed to this feature is poorly reversible. It should be noted that the high-temperature polymorph in the fiber pattern (Figure 8.11) corresponds to the lower-temperature melting peak in Figure 8.8. Since the polymorphic transition is fast on heating, it will always occur prior to melting. As mentioned above, the \textit{i}hPN-Ru polymorph which melts near 190 °C (Figure 8.8) is only observed after isothermal crystallization above 157 °C for approximately a day. For comparison, \textit{ah}PN exhibits a fully reversible crystal-crystal transition from a monoclinic unit cell to a pseudo-hexagonal rotationally disordered crystal structure.\textsuperscript{1,8}
Figure 8.11. Wide-angle x-ray scattering fiber patterns of $i$hPN-Pd: as-drawn fibers at room temperature (top left), after heating to 120 °C (top right), after heating to 140 °C (bottom right), and after cooling from 140 °C to room temperature (bottom left).
The c-axis dimension, or fiber period, can be estimated from the fiber patterns shown in Figures 8.10 and 8.11. Figure 8.12 shows the relationship between the x-ray detector coordinate system (x and y) and the reciprocal lattice coordinates (ζ and ξ). The position of the peaks on the flat plate detector can be converted to ζ and ξ using equations [8.1] and [8.2], where s is the sample-to-detector distance. The ζ coordinate corresponds to the layer height, and ξ is the distance from the origin to the reciprocal lattice point hkl projected into the a*-b* equatorial plane. The c-axis dimension can then be determined from non-equatorial reflections (l ≥ 1) by

\[ c = \lambda l / \zeta \]

where \( \lambda = 1.5418 \text{ Å} \) is the x-ray wavelength.

\[ \xi = \left[ 1 + \frac{1 + (x / s)^2 - 2 \left[ 1 + (x / s)^2 + (y / s)^2 \right]^{1/2}}{1 + (x / s)^2 + (y / s)^2} \right]^{1/2} \]  \hspace{1cm} [8.1]

\[ \zeta = \frac{(y / s)}{\left[ 1 + (x / s)^2 + (y / s)^2 \right]^{1/2}} \]  \hspace{1cm} [8.2]
The fiber patterns of \(i\)hPN and \(s\)hPN show only weak higher-order reflections, as mentioned above, making a definitive assessment of the fiber period difficult. Starting with the \(i\)hPN-Pd observed at 140 °C (Figure 8.11), the \(\zeta\) coordinates of the A’ and C’ peaks are in the ratio of 2:1, indicating that these peaks fall on the 2\(^{nd}\) and 1\(^{st}\) layer lines respectively. Taking the A’ peak as the 002 reflection yields \(c = 11.44\) Å. Assuming that the faint A peaks observed in as-drawn \(i\)hPN-Pd fibers (Figure 8.10) also fall on the 2\(^{nd}\) layer line, the \(c\)-axis dimension is estimated to be 12.07 Å. Finally, the \(c\)-axis dimension of \(s\)hPN is estimated to be 12.36 Å, again assuming the A reflections lie on the 2\(^{nd}\) layer line. Lee and Register found that \(c = 12.420\) Å for
ahPN, in good agreement with the trans zigzag conformation of the fundamental hPN repeat (the projected length of two hPN mers is 12.5 Å).\textsuperscript{1} That the estimated c-axis dimensions of the as-drawn ihPN and shPN fibers are somewhat less than that of ahPN indicates that the chains must be slightly kinked, i.e., the both trans and gauche conformations are present. This is a common occurrence in tactic polymers because the trans zigzag conformation would produce a nonuniform chain cross section, which consequently does not pack efficiently into a regular crystal lattice. Fiber patterns of ahPN exhibit strong reflections on the 5\textsuperscript{th} layer line, which was attributed to a two-backbone-carbon quasi-repeat by Lee and Register.\textsuperscript{1} The patterns of the as-drawn ihPN-Pd and shPN-Ru fiber also show this feature (peaks denoted J in both panels of Figure 8.10), consistent with the slight contraction of the chain configuration inferred from the c-axis dimensions. The pattern of ihPN-Pd at 140 °C (Figure 8.11) shows both the smallest c-axis dimension and the weakest 5\textsuperscript{th} layer line.

\textbf{8.4 Conclusions}

Hydrogenated tactic ring-opened polynorbornenes have been prepared by catalytic hydrogenation of \textit{cis, isotactic} and \textit{cis, syndiotactic} PNs generously provided by the Schrock group at the Massachusetts Institute of Technology. Neither the molecular weight distributions nor the tacticities were affected by hydrogenation. These hPNs provide a unique opportunity to study the effects of tacticity on structure and properties of semicrystalline polymers since the atactic, isotactic, and syndiotactic forms are all semicrystalline. The observed melting point of dynamically crystallized ihPN is above that of ahPN, while shPN unexpectedly melts at a lower temperature than ahPN. The equilibrium melting points of ihPN and shPN are estimated by linear Hoffman-Weeks extrapolation to be 195 °C and 143 °C, respectively, compared to 153 °C
for $a$PN. Isothermally crystallized $i$hPN exhibited bimodal melting for $157 \, ^\circ C \leq T_c \leq 161 \, ^\circ C$. The two melting points are presumed to correspond to distinct crystal structures. The degree of crystallinity was estimated from powder WAXS patterns to be approximately 0.47 and 0.56 for $i$hPN and $s$hPN, respectively. Fiber WAXS patterns clearly demonstrate that $i$hPN, $s$hPN, and $a$hPN each have a distinct crystal structure. In addition, fiber WAXS patterns of $i$hPN-Pd at 140 \, ^\circ C$ revealed a polymorphic transition to a different crystal structure near 133 \, ^\circ C$ on heating. This transition was found to be poorly reversible on cooling. Estimates of the $c$-axis dimensions of the as-drawn $i$hPN and $s$hPN fibers are suggestive of slightly kinked chain conformations.
8.5 References


Chapter 9

Conclusions and Recommendations

9.1 Dissertation Summary

Crystallization is a powerful driver of nanoscale structure in polymers. When semicrystalline blocks are incorporated into block copolymers the interplay between crystallization and block incompatibility gives rise to rich phase behavior. Controlling the strength of block incompatibility with respect to crystallization, such that one of these two mechanisms dominates, provides an opportunity to tune the solid and melt-state morphologies. This thesis explored two systems which lie at opposite ends of this spectrum.

The preparation and performance of a series of thermoplastic elastomers (TPEs) in which the phase behavior is controlled by crystallization was presented in Chapters 4–6. The objective was to provide improved processability over traditional microphase-separated styrenic TPEs by using crystallization and melting to reversibly toggle between the physically cross-linked solid state and a disordered melt. The block sequence motif crystalline-glassy-rubbery was used to target the desired phase behavior while retaining some of the mechanical advantages of glassy hard domains.

Chapter 4 detailed the design and synthesis of block copolymer TPEs with linear low-density polyethylene (E) crystalline blocks, polyvinylcyclohexane (C) glassy blocks, and poly(ethylene-alt-propylene) (EP) rubbery blocks. Two linear block copolymers with the
sequence (E-C-EP)$_2$ were designed to yield disordered melts above the melting point of the crystalline blocks ($T_m$). The phase behavior of the pentablocks was adequately approximated by treating pairs of consecutive blocks (i.e., E-C and C-EP) as diblock copolymers. The limiting block lengths which permit access to homogeneous melts were calculated for each “pseudo-diblock” using the theoretical phase diagram and the experimental segmental interaction parameters ($\chi$).

Polymers were prepared by sequential living anionic polymerization of butadiene, styrene, and isoprene followed by chlorosilane coupling and catalytic hydrogenation. The chlorosilane coupling reaction was dramatically accelerated by adding tetrahydrofuran (THF) concurrently with the coupling agent. Moreover, the living ends were brightly colored in the presence of THF, facilitating precise stoichiometric coupling by monitoring the color of the reaction mixture. This procedure was used with difunctional or hexafunctional coupling agents to prepare symmetric linear or 6-arm star block copolymers, respectively. Star block copolymers prepared by this method were found to degrade during hydrogenation via Si-C bond scission at the core of the star. Degradation was nearly eliminated by adding a few units of butadiene to the end of each arm prior to coupling. The butadiene units serve to minimize the steric strain, stabilizing the core during hydrogenation.

Chapter 5 presented the performance of the linear TPEs. The two linear (E-C-EP)$_2$ pentablock copolymers were found to be disordered above the melting point of the end blocks. Consequently, the viscosities were more than two orders of magnitude less than that of an analogous (C-EP)$_2$ triblock copolymer which remained microphase-separated in the melt. On cooling from the melt, physical cross-links were established in the pentablocks by crystallization. Subsequent aggregation and vitrification of the adjacent C blocks during crystallization limited
the size of the E crystallites. The resulting composite crystalline-glassy hard domains provided reduced Young’s moduli and enhanced breaking strength over the analogous (E-EP)_2 triblock, both of which are desired effects for soft TPEs.

6-arm star TPEs with glassy, crystalline, and composite crystalline-glassy hard domains were presented in Chapter 6. The phase behavior of the 6-arm stars closely tracked that of the analogous linear block copolymers. The star architecture had minimal impact on the small-strain behavior; however, all three types of star TPEs showed enhanced strain hardening above ≈50% strain in comparison to their linear analogs. The 6-arm stars with crystalline end blocks exhibited a 20% increase in the ultimate strength over the analogous linear polymer, while the 6-arm star with glassy end blocks showed a 30% increase. All three types of star block copolymers showed superior recovery and lower hysteresis than the corresponding linear polymers. Star TPEs with crystalline hard domains recovered more rapidly, but showed only modest improvements in the final recovery compared to their linear analogs. In general, the improvements in mechanical performance afforded by the 6-arm star architecture were comparable if not better than those reported in the literature for other branched architectures.

At the other extreme, Chapter 7 described a series of four semicrystalline-rubbery diblock copolymers in which microphase separation preceded crystallization. Upon crystallization, the strongly segregated lamellar morphology exhibited by all four polymers effectively confined the crystallites to the crystallizable domains. Though the semicrystalline morphology remains lamellar, a substantial (and reversible) increase in the domain periodicity was observed upon crystallization. Analysis of wide-angle x-ray scattering patterns of flow-aligned specimens pointed to a crystal texture in which the crystal stems are tilted with respect to the lamellar normals. The tilt angle was found to be larger for higher molecular weight. The crystallites in
the two high molecular weight polymers underwent substantial crystal thickening during isothermal annealing, as assessed by differential scanning calorimetry.

Finally, the implications of tacticity on the structure and properties of hydrogenated polynorbornene (hPN) were discussed in Chapter 8. Purely *isotactic* (*i*) and purely *syndiotactic* (*s*) hPNs were prepared by catalytic hydrogenation of tactic ring-opened polynorbornenes supplied by Prof. Richard Schrock. Hydrogenation had no impact on the molecular weight distribution or tacticity. Both *ihPN* and *shPN* were semicrystalline with distinct crystal structures. Interestingly, the melting points of *ihPN* and *shPN* were found to bracket that of *atactic* hPN; *ihPN* had the highest melting point of the three. In addition, *ihPN* exhibited a polymorphic transition on heating which was not reversible on cooling. Wide-angle x-ray scattering on fiber specimens was used to estimate the *c*-axis dimensions. The as-drawn fibers of *ihPN* and *shPN* exhibit *c*-axis dimensions consistent with slightly kinked backbone conformations.
9.2 Recommendations for Future Work

9.2.1 Thermoplastic Elastomers with Composite Hard Domains

While it is clear that incorporating crystalline and glassy blocks into TPEs offers improvements in processability and mechanical performance, some open questions remain. A better understanding of the role of the glassy blocks during self-assembly and in the solid state is paramount for designing better-performing materials. However, characterizing the glass transition temperature of the glassy blocks is not straightforward because of the heavy overlap between the glass transition and melting/crystallization. Modulated (or dynamic) differential scanning calorimetry (MDSC) may prove useful in separating these features. MDSC is capable of separating the reversing (vitrification, devitrification, and melting) and nonreversing (crystallization) processes.1,2

The optimal relationship between the glass transition temperature of the glassy blocks \((T_g)\) and the melting/crystallization temperatures \((T_m/T_c)\) of the crystalline blocks remains an open question. The \(T_g\) can be adjusted in the polymers prepared by anionic polymerization by using other styrene derivatives, such as methylstyrenes, \(\alpha\)-methylstyrene, or \(t\)-butylstyrene.3 Selective hydrogenation catalysts could also be used to preserve the aromaticity of the styrenic blocks, further expanding the accessible range of \(T_g\) values.4,5 However, changing the identity of the glassy block also changes the segmental interaction parameter against the crystalline and rubbery blocks.4,5 The norbornene-based system studied by Bishop and Register might be better suited to a systematic study of the influence of \(T_g\) on the mechanical performance of TPEs which composite hard domains. Glassy substituted polynorbornenes are available with a range of \(T_g\) values,6 and the structural similarity produces relatively small segmental interaction parameters between various substituted polynorbornenes. Moreover, the mechanical performance of the
crystalline-rubbery-crystalline triblock is much worse than that of (E-EP)\textsuperscript{2}, due to the morphology of highly crystalline \textit{atactic} hPN (the crystalline block of choice). Thus, the mechanical performance of the norbornene-based system is much more sensitive to changes in the glassy block than the TPEs prepared by anionic polymerization described in this work.

The morphology of the TPEs with composite hard domains also requires additional study. More rigorous measures of the solid state structure, such as transmission electron microscopy or neutron scattering with selective deuterium labeling have been suggested, though these analyses would be severely limited by the inherent lack of long-range order. Perhaps the most interesting direction would be to characterize the morphology by small and wide-angle x-ray scattering during deformation, as has been done for styrenic TPEs\textsuperscript{7,8}

Another interesting direction would be to characterize the impact of the star architecture on the mechanical properties of TPEs as a function of hard block content. The anionic-polymerization-based synthetic scheme developed herein provides an excellent platform for such a study. The improvements in ultimate strength are expected to increase with decreasing hard block content. The star block copolymers reported in Chapter 6 show significant variability in the measured mechanical properties. The variability likely stems from the compression molding process of preparing specimens for mechanical testing. More consistent results might be obtained from solvent-cast specimens\textsuperscript{9}
9.2.2 Crystalline-Rubbery Diblock Copolymers

Many interesting questions arise from the results presented in Chapter 7. First of all, a definitive assignment of the crystal orientation would require pole figure analysis. The orientation of the ahPN determined by simple wide-angle x-ray scattering on oriented specimens is generally consistent with that of poly(ethylene oxide) in glassy microdomains, raising the possibility that the crystal orientation may depend on the crystallization conditions. Provided that the hypothesized orientation is correct, the surface energy term in the Gibbs-Thomson analysis contributes the greatest uncertainty to the crystal thickness calculations. Transmission electron microscopy (TEM) on microtomed sections of flow-aligned specimens may permit a direct measurement of the crystallite orientation and thickness. The hydroxyhexafluoroisopropyl moiety in the rubbery block may also be leveraged to provide contrast. In addition, measurements of macroscopic dimensional changes of flow aligned specimens, particularly in the load direction, may be able to provide insight into the mechanism(s) responsible for the large domain spacing change upon crystallization. Simultaneous time-resolved small and wide-angle x-ray scattering could also be used to elucidate the relationship between the crystallization process and the change in d-spacing.

9.2.3 Hydrogenated Tactic Polynorbornenes

The crystal structures of ihPN and shPN may be obtained from the fiber scattering patterns presented in Chapter 8. The c-axis dimensions have been estimated from the 2nd layer lines. Estimates of the a and b-axis dimensions may be obtained from the positions of the equatorial reflections by graphical methods, such as a Hull-Davey chart. Attempts at applying these methods to ihPN have been inconclusive thus far because only a few equatorial
reflections are available. In the case of shPN, initial attempts to match the scattering peaks to a Hull-Davey chart for a rectangular lattice were unsuccessful. Additional information may be garnered from tilted fiber patterns which can accentuate weak diffraction spots.\textsuperscript{10,11} Better oriented fibers may also be obtained by drawing from solution. Determining the full atomic coordinates would require modeling software such as Cerius\textsuperscript{2} (Accelrys Inc.).

More accurate estimates of the equilibrium melting points, as well as the crystal fold surface energies, can be obtained from a Gibbs-Thomson analysis. This analysis requires measuring the crystal thicknesses (by small-angle x-ray scattering) and melting points of each tactic hPN crystallized under various conditions. In addition, the subject of polymorphism in IhPN requires further investigation. The crystal structure of the IhPN polymorph which melts near 190 °C has not been characterized. It has yet to be seen whether a sample exhibiting only this polymorph can be prepared. A powder diffraction pattern of a specimen exhibiting both polymorphs, such as those observed by DSC, may prove sufficient. Otherwise a self-seeded crystallization approach may be useful: a sample exhibiting both polymorphs would be partially melted to remove the lower-melting crystals and then recrystallized; the hope is that the molten material will add to the existing crystals of the higher-melting polymorph rather than nucleating new crystals.
9.3 References


Appendix A

Hydrogenated Poly(hydroxyhexafluoroisopropynorbornene)

Ring-opening metathesis polymerization of HFAN has only recently been reported,\(^1\) so some basic characterization of homopolymer hydrogenated poly(hydroxyhexafluoroisopropynorbornene) (hPHFAN) was required for a detailed analysis of the hP(N-HFAN) diblock copolymers. As noted in Chapter 7, the synthesis of PHFAN was readily accomplished using the 1\(^{st}\) Generation Grubbs initiator with 5 molar equivalents of tricyclohexylphosphine. The gel permeation chromatography (GPC) trace of the as-synthesized polymer (Figure A.1) shows a narrow molecular weight distribution. Hydrogenation was accomplished using Pd/CaCO\(_3\); assuming no loss of the hydroxyl groups the degree of saturation of the olefinic backbone bonds was calculated to be 99.8\% by \(^1\)H NMR in THF-d\(_8\). The GPC trace of hPHFAN (Figure A.1) revealed that the hydrogenation reaction proceeded without any sign of chain scission, as expected for the catalytic hydrogenation of substituted polynorbornenes.\(^2\)
Figure A.1. GPC traces of the unsaturated PHFAN precursor ($M_L = 46.8$ kg/mol and $D = 1.16$) and hydrogenated hPHFAN-47 ($M_{calc} = 47.1$ kg/mol and $D = 1.17$). The shift in elution time is attributed to a reduction in the hydrodynamic volume upon saturation.²

The glass transition temperature ($T_g$) of the hydrogenated homopolymer hPHFAN-47 was determined to be 45 °C by differential scanning calorimetry (DSC) on heating at 10 °C/min, as shown in Figure A.2. Consequently, although hPHFAN is glassy at room temperature, it is rubbery in the temperature range at which hPN crystallizes. The density of hPHFAN-47 was measured to be $\rho(23$ °C) = 1.3404 ± 0.0007 g/cm³ by William Mulhearn using a density gradient column. A linear gradient was established using mixtures of Ca(NO₃)₂ in DI water and calibrated with glass floats. The thermal expansion coefficients in the glassy and rubbery regimes were measured using spectroscopic ellipsometry³,⁴ (J.A. Woollam M-2000) on a ≈260 nm thick film of hPHFAN-47 supported on a silicon wafer bearing the native oxide layer. The
film was prepared by spin coating from THF and was annealed above \( T_g \) overnight. The thickness data, \( h(T) \), were fit to:

\[
\ln(h(T)) = \ln(h_{ref}) + \alpha(T - T_{ref})
\]

[A.1]

where \( h_{ref} \) is the thickness at \( T_{ref} \), \( \alpha \) is the thermal expansion coefficient, and \( T_{ref} = 160^\circ \text{C} \). The measured thicknesses and fits to equation [A.1] in the glassy and rubbery regimes are shown in Figure A.3. The thermal expansion coefficients measured by ellipsometry were corrected for the thermal expansion mismatch between the polymer and substrate as described by Pye and Roth.\(^4\) This method is reported to yield good agreement with the volumetric thermal expansion coefficient measured by dilatometry for polystyrene.\(^4\) The corrected bulk thermal expansion coefficients in the glassy and rubbery regimes were determined to be \( \alpha_g = 2.34 \times 10^{-4} \text{ K}^{-1} \) and \( \alpha_r = 5.98 \times 10^{-4} \text{ K}^{-1} \), respectively, with. The intersection between the fits gives \( T_g = 51^\circ \text{C} \). The specific volume \((v = 1/\rho)\) correlations for hPHFAN given in equations [A.2] and [A.3] were formulated by substituting \( v \) for \( h \) in equation [A.1]; \( v \) was calculated at \( T_{ref} = 160^\circ \text{C} \) using \( \rho(23^\circ \text{C}) \) and the corrected bulk thermal expansion coefficients.

\[
\text{Glassy regime: } \ln(v_g(T)) = -0.2609 + 2.34 \times 10^{-4}(T - 160^\circ \text{C}) \\
\text{Rubbery regime: } \ln(v_r(T)) = -0.2212 + 5.98 \times 10^{-4}(T - 160^\circ \text{C})
\]

[A.2] [A.3]

These correlations, along with PVT data for hPN,\(^5\) were used to convert weight fractions (determined by \(^1\text{H} \) NMR spectroscopy) to volume fractions for the hP(N-HFAN) diblock copolymers. The electron density difference between hPHFAN and semicrystalline hPN was estimated to be \( \Delta\rho_e \approx 80 \text{ e}^{-/\text{nm}^3} \) at 100 °C, compared to \( \Delta\rho_e \approx 25 \text{ e}^{-/\text{nm}^3} \) for crystalline-amorphous hPN, corresponding to an order of magnitude difference in SAXS contrast (the small-angle x-ray scattering intensity is proportional to \( \Delta\rho_e^2 \)).\(^6\)
Figure A.2. DSC trace of hPHFAN-47 on heating at 10 °C/min after cooling from the melt at 10 °C/min.

Figure A.3. Ellipsometry trace of hPHFAN-47 showing fits to the glassy and rubbery regions used to determine the thermal expansion coefficients.
Appendix A References


Appendix B

Crystal Orientation in Crystalline-Rubbery Diblock Copolymers

The following procedure\textsuperscript{1-3} was used to calculate the split angles between wide-angle x-ray scattering (WAXS) peaks as a function of the crystal orientation for hydrogenated polynorbornene (hPN) in flow-aligned diblock copolymers. Sharp diffraction peaks are observed when Bragg’s law is satisfied:

\[
\frac{\mathbf{\hat{p}}_{hkl} \cdot \mathbf{\hat{b}}_N}{|\mathbf{\hat{p}}_{hkl}|} = \cos(90 - \theta_{hkl}) \tag{B.1}
\]

where \(\mathbf{\hat{p}}_{hkl}\) is the vector normal to the \((hkl)\) scattering planes, \(\mathbf{\hat{b}}_N\) is the unit vector denoting the direction of the incident x-rays, and \(\theta_{hkl}\) is half of the scattering angle (in degrees). If equation [B.1] is satisfied, the split angle between diffraction peaks (\(\psi\)) can be calculated by projecting the scattering vector onto the plane of the detector. For example, if \(\mathbf{\hat{b}}_N = \mathbf{\hat{x}}\) and the detector is the \(\mathbf{\hat{y}} - \mathbf{\hat{z}}\) plane as shown in Figure B.1, the split angle is given by equation [B.2].

\[
\tan\left(\frac{\psi}{2}\right) = \frac{|\mathbf{\hat{p}}_{hkl} \cdot \mathbf{\hat{z}}|}{|\mathbf{\hat{p}}_{hkl} \cdot \mathbf{\hat{y}}|} \tag{B.2}
\]
Figure B.1. Schematic of the azimuthal split angle ($\psi$) between diffraction spots projected onto the $\hat{y} - \hat{z}$ detector plane.

The vector $\vec{\rho}_{hkl}$ is conveniently expressed in terms of the crystallographic basis vectors in reciprocal space $\hat{a}^*$, $\hat{b}^*$, and $\hat{c}^*$ by equation [B.3], where $a^*$, $b^*$, and $c^*$ are the reciprocal unit cell dimensions.$^{1,2,4}$

$$\vec{\rho}_{hkl} = ha^* \hat{a}^* + kb^* \hat{b}^* + lc^* \hat{c}^*$$  \hspace{1cm} [B.3]

The magnitude of $\vec{\rho}_{hkl}$ is the interplanar spacing, $|\vec{\rho}_{hkl}| = d_{hkl}$. It is important to note that the unit cell of the rotationally ordered polymorph of hPN (the stable polymorph below $\approx$100 °C) is monoclinic$^5$ (Figure B.2), so $\hat{a}^*$, $\hat{b}^*$, and $\hat{c}^*$ are not orthonormal.
Figure B.2. Schematic of the monoclinic hPN unit cell\textsuperscript{5} (top), and the relationship between the $a$ and $c$ axes in real space and the $a^*$ and $c^*$ axes in reciprocal space (bottom). The $b$ and $b^*$ axes are coincident and perpendicular to the $a$-$c$ (and $a^*$-$c^*$) plane. By convention the crystal stems lie along the $c$-axis.

The crystallite orientation is deduced by postulating the relationship between the crystal lattice and the $x$, $y$, $z$ coordinate system, computing the expected split angles using equations [B.1] and [B.2], and comparing the calculated $\psi$ to the experimental WAXS patterns. For

\[
\begin{align*}
\beta^* &= 180^\circ - \beta \\
\beta &= 130.7^\circ \\
a &= 6.936 \text{ Å} \\
a^* &= 1/(a \sin \beta) \\
b &= 9.596 \text{ Å} \\
b^* &= 1/b \\
c &= 12.420 \text{ Å} \\
c^* &= 1/(c \sin \beta)
\end{align*}
\]
consistency \( \hat{x} \) is defined as the unit vector in the constraint direction (CD), \( \hat{y} \) is the flow direction (FD), and \( \hat{z} \) is the load direction (LD). An initial orientation of the crystallites is postulated and \( \hat{a}^* \), \( \hat{b}^* \), and \( \hat{c}^* \) are expressed in terms of \( \hat{x} \), \( \hat{y} \), and \( \hat{z} \). To allow for all possible orientations the crystallographic axes are tilted by an angle \( \lambda \) with respect to \( \hat{z} \) about the y-axis. Two situations give rise to tilt: (1) the unit cell is inclined with respect to the microdomain normal \( \mathbf{n} \) which is perpendicular to the fold surfaces (referred to as unit cell tilt), or (2) either the crystal fold surfaces are tilted with respect to \( \mathbf{n} \) or \( \mathbf{n} \) is rotated about the FD (referred to as lamellar tilt). Figure B.3 shows schematic representation of both scenarios. The tilt is applied by multiplying each of the crystallographic axes (expressed in terms of \( \hat{x} \), \( \hat{y} \), and \( \hat{z} \)) by the rotation matrix [B.4].

\[
R_y(\lambda) = \begin{bmatrix}
\cos(-\lambda) & 0 & \sin(-\lambda) \\
0 & 1 & 0 \\
-\sin(-\lambda) & 0 & \cos(-\lambda)
\end{bmatrix}
\]
**Figure B.3.** Schematics of generic reciprocal lattice vectors before (light blue) and after (dark blue) rotation and the lamellar normal ($n$, red) with respect to the real-space coordinate system (dotted, gray). The top panel shows tilt ($\lambda$) in the $x$-$z$ plane. Rotations ($\gamma$) giving rise to unit cell tilt and lamellar tilt are shown in the middle and bottom panels, respectively.
Free rotation about $\vec{n}$ is accounted for by the angle $\gamma$. If the scenario includes unit cell tilt
the crystallographic axes are rotated about $\hat{z}$ by multiplying the crystallographic basis vectors
by:

$$ R^{\vec{n}}(\gamma) = \begin{pmatrix} \cos(\gamma) & -\sin(\gamma) & 0 \\ \sin(\gamma) & \cos(\gamma) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{[B.5]} $$

If $\lambda$ corresponds to tilt of the lamellae, then the crystallographic axes are rotated around the unit
vector $\vec{n} = (u, v, w)$. This transformation is more involved and requires first rotating the entire
coordinate system such that $\vec{n}$ is parallel to $\hat{z}$, then rotating around $\hat{z}$ by $\gamma$, and finally restoring
the tilted position of $\vec{n}$. These operations are achieved by multiplying the crystallographic axes
by expression [B.6].

$$ T^{-1} = \begin{pmatrix} u / \sqrt{u^2 + v^2} & v / \sqrt{u^2 + v^2} & 0 \\ -v / \sqrt{u^2 + v^2} & u / \sqrt{u^2 + v^2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{[B.6]} $$

$$ T = \begin{pmatrix} w & 0 & -\sqrt{u^2 + v^2} \\ 0 & 1 & 0 \\ \sqrt{u^2 + v^2} & 0 & w \end{pmatrix} \quad \text{[B.7]} $$

For each value of $\lambda$ between $-180^\circ$ and $180^\circ$, $\gamma$ is calculated to satisfy the Bragg condition [B.1]
in each view (i.e., $\vec{b}_N = \hat{x}$, $\hat{y}$, and $\hat{z}$). The split angle is then calculated using equation [B.2].

Before presenting the results of the calculations, the experimental WAXS patterns must
be discussed. The alignment quality is highest for hP(N-HFAN)-17 and hP(N-HFAN)-43, so the
discussion will focus on these polymers. The (020) peaks of all four polymers in all three views

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exhibited $\psi = 0^\circ$. The azimuthal traces of the (110) peaks of both hP(N-HFAN)-17 and hP(N-HFAN)-43, showed evidence of multiple overlapping peaks, particularly in the CD view. This may be attributable to multiple crystal orientations with respect to the microdomains, or a single orientation of the crystallites with rotation of the microdomains about FD. The relative intensities of the (110) peaks with different $\psi$ depends not only on the proportion of crystallites with a given tilt ($\lambda$), but also on the prevalence of the particular rotational orientation ($\gamma$) which meets the Bragg condition. Thus, the proportion of crystallites with a particular tilt cannot be ascertained from the available information. For hP(N-HFAN)-17, the dominant (110) split angle $\psi = 38^\circ$ is considered. In the case of hP(N-HFAN)-43, the (110) azimuthal traces appear to comprise two overlapping peaks with $\psi \approx 70^\circ$ and $120^\circ$. 
Figure B.4. Example 2D WAXS pattern of hP(N-HFAN)-43 in the CD view (a). The azimuthal angle is defined in the counterclockwise direction from the 3 o’clock position (0°). Azimuthal traces of the (020) peaks of hP(N-HFAN)-43 (b) and the (110) peaks of hP(N-HFAN)-43 (c) and hP(N-HFAN)-17 (d). The meridian (azimuth = 90° and 270°) corresponds to LD in both the CD and FD views. In the LD view the meridian is CD.
Six scenarios were investigated using the procedure outlined above. Myers and Register found that LPE crystallites confined to lamellar microdomains were oriented with \(a\)-axis normal to the interfaces.\(^{3,8}\) This configuration allows the crystal thickness (\(c\)-axis) to exceed the thickness of the microdomains and places the fast growth direction (\(b\)-axis) in plane. The fast growth direction is not known for hPN, so orientations with the \(c\)-axis in plane and either \(a^*\) or \(b^*\) normal to the interfaces were investigated. The calculations for \(a^* \parallel \hat{z}\) including unit cell tilt or lamellar tilt are shown in Figure B.5. Lamellar tilt cannot produce the observed \(\psi\) for the (110) peaks in the CD view for either hP(N-HFAN)-17 or -43. In the FD view any value of \(\psi\) is possible; however, a single value of \(\lambda\) cannot account for the observed splitting for both the (020) and (110) peaks. The same problem arises if the unit cell is tilted. Thus, this orientation is not consistent with the experimental WAXS patterns. Keeping the crystal stems in-plane with \(b^* \parallel \hat{z}\) and allowing for lamellar tilt fails to meet the Bragg condition for the (020) planes under any circumstances. Using the same initial orientation with unit cell tilt gives \(\psi \approx 90^\circ\) (i.e., peaks on the meridian) for all \(\lambda\), which is inconsistent with the observed equatorial (020) peaks. Clearly this crystal texture is also incorrect.
Figure B.5. Results of the split angle calculations in the CD view (black) for the (020) and (110) peaks with \( a^* \) normal to the interfaces with lamellar tilt (a) or unit cell tilt (b) and the measured \( \psi(110) \) for hP(N-HFAN)-17 (blue) and hP(N-HFAN)-43 (red).

Based on the results above, the crystal stems do not lie in the plane of the microdomain interfaces. This orientation has been observed under certain conditions for confined crystallization of poly(ethylene oxide) (EO) in block copolymer microdomains.\(^9\)\(^{-11}\) Placing the \( c \)-axis parallel to \( \hat{z} \) and accounting for lamellar tilt can give rise to any value of \( \psi \) in all of the three views (Figure B.6). However, this texture is equivalent to the well-known fiber orientation,\(^1\)\(^,\)\(^2\)\(^,\)\(^4\) and gives the same split angle for all reflections with a common value of \( l \) (i.e., \( \psi(020) = \psi(110) \) for all \( \lambda \)). If instead the unit cell is tilted about the \( b \)-axis with respect to \( \hat{n} \),
$\psi(020) = 0^\circ$ for all $\lambda$ and the (110) split angles measured by WAXS can be accounted for in both polymers by invoking different tilt angles.

Figure B.6. Results of the split angle calculations in the CD view (black) for the (020) and (110) peaks with $c$ normal to the interfaces with lamellar tilt (a) or unit cell tilt (b) and the measured $\psi(110)$ for hP(N-HFAN)-17 (blue) and hP(N-HFAN)-43 (red).

The $c$-axis tilted about $b$ is the only orientation considered which can produce the observed split angles in the CD and FD views of both hP(N-HFAN)-17 and hP(N-HFAN)-43; however, some additional observations need to be reconciled. For one, the CD views show multimodal (110) reflections. In addition, both polymers show Bragg peaks in the LD view. If the lamellar orientation were perfect the (020) and (110) reflections should not appear in the LD
view. These additional reflections could arise from two situations: (1) there are two (or more) populations of crystallites with distinct orientations with respect to the microdomains, or (2) all of the crystallites have the same orientation with respect to the microdomains, but some of the lamellae are rotated about LD. The breadth of the primary SAXS peak in the FD view (Figure 7.4) suggests the latter situation. Moreover, the melting endotherms are monomodal and do not show evidence of multiple distinct crystallite populations (Figure 7.3). To test whether this is a plausible explanation for the experimental observations the unit cell tilt was fixed and then a lamellar tilt about FD was applied. hP(N-HFAN)-17 shows one dominant set of reflections with $\psi(110) = 38^\circ$, assuming that this corresponds to the population of crystallites which reside in the majority lamellae ($n \parallel LD$) the $c$-axis tilt is calculated to be $\lambda \approx 21^\circ$. Fixing the $c$-axis tilt at $21^\circ$ and allowing for rotation of the lamellae about FD can produce any value of $\psi(110) > 32^\circ$ (Figure B.7). In the FD view, all values of $\psi(110)$ are allowed, which might explain the appearance of a single broad peak in the FD scattering pattern. Rotation of the lamellae also produces nonzero values of $\psi(020)$; in the experimental patterns the (020) peaks lie on the equator, but the presence of lamellar tilt cannot be ruled out on this basis. Therefore, a single orientation of the crystallites with lamellar tilt can account for the observed WAXS patterns of hP(N-HFAN)-17.
Figure B.7. Azimuthal traces of the (110) reflections of hP(N-HFAN)-17 in the CD (meridian is FD) (a) and LD (meridian is CD) (b) views. The primary peak positions are indicated by triangles. Shaded regions represent disallowed peak positions assuming a \(c\)-axis tilt of 21° and free rotation of the lamellae about FD.

Analysis of hP(N-HFAN)-43 is less straightforward since there appears to be two equally intense sets of (110) reflections in the CD view. Choosing the set of peaks with \(\psi \approx 70°\) gives a \(c\)-axis tilt of \(\approx 40°\) about \(b\), which places both \(a\) and \(b\) in the plane of the microdomains. Fixing the \(c\)-axis tilt with respect to \(n\) at 40° and allowing for tilt of the lamellae about FD can again account for all of the observed reflections in all three views (Figure B.8). All \(\psi(110) > 66°\) are allowed in the CD and LD views, which is consistent with the observation that the minimum intensity in the (110) azimuthal trace occurs at 0° and 180°. Choosing instead the set of peaks with \(\psi = 120°\) gives a \(c\)-axis tilt of 75°. It is interesting to note that this orientation would place \(c\) inclined just 15° from the lamellar plane, nearly recovering the orientation observed for LPE under lamellar confinement. Subsequently allowing lamellar tilt gives rise to Bragg peaks with \(\psi > 115°\), excluding a large portion of the observed intensity. Therefore, without invoking
multiple crystal orientations, a 40° tilt of the $c$-axis with respect to $n$, and rotation of $n$ about FD is the only orientation examined which can account for all of the observations by WAXS.

Figure B.8. Azimuthal traces of the (110) reflections of hP(N-HFAN)-43 in the CD (meridian is FD) (a) and LD (meridian is CD) (b) views. The primary peak positions are indicated by triangles. Shaded regions represent disallowed peak positions assuming a $c$-axis tilt of 40° and free rotation of the lamellae about FD.
Appendix B References


Appendix C

Publications from this Dissertation

