Synthesis and Phase Behavior of Tetrablock Terpolymers

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To my family
Abstract

Block copolymers are macromolecules formed by covalently joining two or more distinct polymer blocks that may be thermodynamically incompatible. The incompatibility drives segregation of the individual blocks on the molecular scale (5 – 100 nm), producing extraordinarily varied and complex morphologies. This thesis describes the synthesis and phase behavior characterization of tetrablock terpolymers composed of poly(styrene) (S), poly(isoprene) (I), and poly(ethylene oxide) (O) with an emphasis on ABAC-type polymers. Motivated by SCFT calculations, investigation into the phase behavior of sphere-forming SIS’O tetrablocks led to the identification of multiple ordered structures upon varying the symmetry parameter \( \tau = N_S/(N_S + N_{S'}) \), where \( N \) is the block degree of polymerization. Complementary data from dynamic mechanical spectroscopy, small angle X-ray scattering, and transmission electron microscopy yielded evidence for nine different spherical phases: FCC, HCP, BCC, rhombohedral (tentative), liquid-like packing, dodecagonal quasicrystal, and Frank–Kasper \( \sigma \) and A15, and simple hexagonal packing (HEX\(_S\)). Close to the order-disorder transition, equilibrium morphologies are formed due to facile chain exchange between micelles. Transition to non-equilibrium behavior occurred several tens of degrees below the order-disorder transition where increased segregation strength between the O core and SIS’ corona arrests chain exchange between domains. Structure and thermodynamic stability of the HEX\(_S\) phase were examined in greater detail and the phase was found to be especially stable in low-\( \tau \) samples. Switching the block sequencing from SISO to ISIO led to an extinguishment in complex behavior as only BCC and hexagonally packed cylinders (HEXC) were identified as ordered phases. The decrease in morphological complexity was attributed to the formation of frustrated interfaces as the ISIO molecular architecture mandates contact between the most thermodynamically incompatible I and O blocks. Additionally, synthetic strategies capable of producing ABCA’-type tetrablocks with asymmetrically sized corona chains were developed. These results expand the monomer toolkit capable of producing new types of block polymers and provide a deeper glimpse into the fundamental principles that guide block polymer phase behavior.
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1.1 Motivation

In only a few decades, polymers have become ubiquitous in daily life and now represent one of the most important material classes. The distinguishing feature of a polymer is its high molecular size which endows the macromolecule with unique chemical and physical properties. Synthetic polymers are made by covalently linking subunits called monomers through the process of polymerization. Physical properties of the resulting polymer are primarily determined by the starting monomers. For example, poly(styrene) (PS) is a rigid, transparent solid at room temperature while poly(isoprene) (PI) is a viscous liquid. PS is brittle but has a high elastic modulus while PI can be extended to high strains without failure but has a low modulus. A blend of both homopolymers might retain the attractive properties of each constituent while offsetting the undesirable ones. This is analogous to the behavior seen in intermetallics where, for example, copper and zinc can be combined to form a single phase known as brass which is mechanically superior to either component. However, when blended, most polymers macrophase separate even when their monomers are miscible. This limitation is easily explained through the use of Flory-Huggins theory, an extension of regular solution theory to the case of polymer-polymer blends. This theory was independently derived by Flory and Huggins more than 70 years ago for mixing random-walk chains on an
incompressible lattice. Using this, the Gibbs free energy of mixing two polymers becomes:\(^1\)

\[
\frac{\Delta G_m}{kT} = \frac{f_A}{N_A} \ln(f_A) + \frac{f_B}{N_B} \ln(f_B) + f_A f_B \chi_{AB}
\]  

where \(f_A\) and \(f_B\) are the volume fractions of the constituent homopolymers, \(k\) is the Boltzmann constant, \(T\) is the temperature, and \(\chi_{AB}\) is the Flory-Huggins interaction parameter for the polymers A and B having degree of polymerization \(N_A\) and \(N_B\), respectively. The first two terms on the right-hand side represent the combinatorial entropy of mixing (\(\Delta S_m\)) while the last term accounts for the enthalpic contribution (\(\Delta H_m\)). In the case of polymers (large \(N_A\) and \(N_B\)), the entropic contribution is vanishingly small and enthalpic considerations dominate phase behavior. Therefore, even a small positive value of \(\chi_{AB}\) drives macrophase separation in polymer blends.

Figure 1.1 Illustration of a linear diblock copolymer made by covalently linking homopolymers of poly(styrene) and poly(isoprene).

Block polymers (Figure 1.1) overcome this limitation by covalently linking homopolymers of distinct monomers into a single macromolecule. Though this avoids macrophase separation, a delicate balance between the entropic and enthalpic forces leads to microphase separation and the formation of a rich variety of structured morphologies. A classic example is poly(styrene)-\(b\)-poly(isoprene)-\(b\)-poly(styrene) (SIS), composed of covalently linked PS and PI blocks. Commercially, this polymer is part of the Kraton family which has enormous industrial and practical significance in the fields of impact toughening, pressure sensitive adhesives, and packaging. These applications draw
directly from the ability of the polymer to microphase separate and form hard poly(styrene) domains which are physically crosslinked by soft, rubbery poly(isoprene) chains endowing the structure with both high tensile strength and elasticity. The design opportunities continue to expand with high technology applications in semiconductor devices, controlled drug delivery, membranes with tunable nanochannels, and nanolithography.

Despite these advances and the tantalizing technological prospects, the complexity associated with exploring more complex molecular architectures (AB vs. ABCA) and topologies (linear vs. branched) poses a daunting challenge. Amongst other factors, block polymer phase behavior is largely influenced by the number of blocks \( n \) and the number of block types \( k \). It is hypothesized that every \( (n,k) \) enumeration has the ability to produce a unique material.\(^{11}\) Exploiting the full potential of block polymer utility requires a synergistic approach combining innovative chemistry with advancements in theoretical predictive tools and structural characterization methods. Thus, manipulating the self-assembly of these fascinating materials requires the collaborative effort of various fields with the goal of understanding fundamental interactions between blocks and developing computational tools to predict these behaviors \( a \ priori \).

Towards this end, this thesis presents experimental and theoretical research in tetrablock terpolymer \((n = 4, k = 3)\) synthesis and self-assembly. These results extend the synthetic toolkit capable of producing new types of block polymers, explore new self-assembled structures, and give a deeper glimpse into the fundamental principles that guide block polymer phase behavior.

\section*{1.2 Block polymer phase behavior}

More than 60 years ago, living anionic polymerization enabled the production of well-defined polymers by eliminating undesired termination or chain-transfer steps.\(^{12}\) Refinement of anionic polymerization and other chemistries,\(^{1,13-15}\) and the ability to perform sequential monomer addition, has enabled facile production of a variety of block polymers. Advancements in the understanding of linear block copolymer phase behavior
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through complementary use of theory and experiment are reviewed in the following sections.

1.2.1 Diblocks

In order to understand diblock phase behavior, a deeper understanding of the Flory-Huggins interaction parameter is required. Within the context of Flory-Huggins theory, $\chi_{AB}$, or simply $\chi$, is a dimensionless measure of the energetic penalty for exchanging a repeat unit of polymer A with that of polymer B. Assuming Van der Waals forces are the only interactions, $\chi$ is always positive and varies inversely with temperature. If these dispersive interactions are short range and isotropic, $\chi_{AB}$ can be estimated following a solubility parameter approach as

$$\chi = (V/RT)(\delta_A - \delta_B)^2$$

where $V$ is the repeat unit molar volume, $R$ is the gas constant and $\delta_i$ are the relevant solubility parameters. Since $\chi$ is derived from a lattice based theory, the magnitude of the interaction parameter (and $V$) is dependent on the chosen lattice size. Practically, these estimates can be remarkably poor and instead, experimental data is typically described through the following empirical formula:

$$\chi = \alpha/T + \beta.$$ Both $\alpha$ and $\beta$ are constants where $\beta$ accounts for the excess, non-combinatorial entropy of mixing. Figure 1.2 shows solubility parameters for several monomer pairs emphasizing that differences in the chemistry lead to a higher value of the interaction parameter and increased immiscibility between the constituent polymers.

The compound variable $\chi N$ is an important quantity known as the segregation strength. A higher $\chi$ increases the enthalpic cost of interfacial contact between different blocks while increasing $N$ causes loss of translational and configurational entropy. Therefore, qualitatively speaking, low values of $\chi N$ lead to a disordered phase dominated by entropic interactions while increasing $\chi N$ results in ordered phases. Conversely, increasing temperature (decreasing $\chi$) causes the diblock polymer system to undergo an order to disorder transition (ODT). The diblock morphology observed within the ordered phase is dictated by the block volume fraction. The segregation strength can be divided into three regimes: strong segregation limit (SSL), weak segregation limit (WSL), and intermediate segregation region (ISR). Though there is no sharp demarcation between these regimes, the WSL ($\chi N \sim 10$) is characterized by fluctuations which are local, transient
deviations in composition from the bulk value arising from random thermal motion within the material. As $\chi N$ is increased, individual chains become significantly perturbed from their Gaussian configurations, signaling a transition from WSL to ISR. On the other extreme, the SSL is characterized by pure block polymer domains and narrow interfacial regions ($\chi N >> 10$). Early theoretical work was carried out independently in the two asymptotic limits, WSL and SSL.

The essential competition between enthalpy (interfacial tension) and entropy (chain stretching) which dictates block polymer phase behavior was first captured by Meier in his theory presenting the formation of spherical domains in AB diblock copolymers. Helfand and co-workers built on this foundation by incorporating various effects and making the theory more quantitative. They adapted self-consistent mean field theory (SCFT), first utilized by Edward to study the excluded volume effect, in order to yield quantitative estimates for domain periodicities in the lamellar phase. The domain size was obtained by minimizing free energy contributions from interfacial tension,
1.2 Block polymer phase behavior

localization of block joints at the interface, and entropy loss due to chain stretching. These results were subsequently extended to treat spherical\textsuperscript{27} and cylindrical\textsuperscript{28} domains. However, the utilization of a narrow interface approximation caused the theory to only be valid in the SSL. Consequently, the theory was unable to treat phase transitions near the ODT and thermally induced order-order transitions (OOTs).\textsuperscript{29}

Phase behavior in the WSL was addressed by the seminal work of Leibler in 1980 who developed the phase portrait of an AB diblock near the ODT in the mean field ($N \rightarrow \infty$) limit.\textsuperscript{30} Leibler applied de Gennes’ random phase approximation (RPA) for polymer melts\textsuperscript{31} to the case of a monodisperse diblock melt and found a critical point at $(\chi N)_{c} \approx 10.5$ and $f_{A,c} = 0.5$. At this point, upon heating the diblock underwent a second-order phase transition from a homogenous melt to an ordered one-dimensional lamellar phase (LAM). Only two additional phases were found to be stable near the ODT: two-dimensional hexagonally ordered cylinders (HEXC) and a three-dimensional body-centered-cubic (BCC) arrangement of spheres (Figure 1.3). Later, Matsen and Schick solved the complete set of SCFT equations numerically, avoiding the use of RPA, to construct a phase diagram of AB diblock polymers examining the stability of all the previously reported phases (LAM, HEXC, and BCC) and the gyroid network phase (GYR).\textsuperscript{32} Though the mean-field nature of the theory makes it less accurate near the ODT, SCFT has proven remarkably successful in calculating the relative stability of competing ordered phases.\textsuperscript{11,33} The SCFT framework continued to be refined by many theorists, notably Matsen and co-workers,\textsuperscript{34–37} who were able to unify the theories describing block copolymer phase behavior in the SSL and WSL regimes.\textsuperscript{35,38–40}

Despite its successes, Leibler’s analysis was valid only in the case of infinitely long chains and neglected fluctuation effects which have been experimentally shown to be important in any practical, finite molecular weight polymer.\textsuperscript{41–43} Fredrickson and Helfand used the Hartree approximation employed by Brazovskii\textsuperscript{44} in order to incorporate fluctuation effects and concluded the ODT in a symmetric diblock was actually a weakly first-order transition.\textsuperscript{45} They predicted the location of the ODT was $(\chi N)_{ODT} = 10.495 + 41.022\bar{N}^{-1/3}$, where $\bar{N}$ is an invariant degree of polymerization which
characterizes the amount of overlap between chains. The Fredrickson-Helfand (FH) theory was successful in capturing some additional qualitative aspects of the ODT including direct transitions from the disordered state to cylinders but is strictly valid only beyond $N > 10^9$. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights. Variations and improvements to FH theory continued to be developed but have yet to be widely accepted as they cannot quantitatively predict the behavior of polymers of typical molecular weights.

Despite initial conflicting reports, experimentalists confirmed the existence of the now ubiquitous BCC phase in diblock melts in 1982. The three classical morphologies (LAM, HEXC, BCC) were expanded by the identification of several new morphologies. The ordered bicontinuous double diamond (OBDD) phase was first reported in star and later in linear block copolymers. However, this was an erroneous assignment due to overreliance on TEM as scattering experiments confirmed the
1.2 Block polymer phase behavior

![Figure 1.4](image)

**Figure 1.4** (a) Theoretical and (b) experimental diblock copolymer phase portraits. $S_{cp}$ represents the region where close-packed phases (FCC/HCP) are predicted to be stable. The experimental phase portrait was constructed through characterization of poly(styrene)-b-poly(isoprene) diblocks. Adapted from Matsen, M.W., *J. Phys. Condens. Matter*, 14, R21-R27. Copyright IOP Publishing. Reproduced with permission. All rights reserved.

morphology to be the gyroid phase after this phase was discovered in poly(styrene)-b-poly(2-vinylpyridine) mixture and a poly(styrene)-b-poly(isoprene) diblock. Another complex phase called hexagonal perforated lamellae (HPL), characterized by a hexagonal arrangement of passages in the lamellar layer of the minority phase, was discovered but shown to be metastable. As an example of the fruitful collaboration required between theory and experiments, SCFT simulations first anticipated the presence of another network phase in diblocks called $O$ and were experimentally confirmed just a few years later. Further experiments clarified that the $O$ phase exists as an equilibrium phase in the tested poly(styrene)-b-poly(isoprene) system. All classical and complex phases highlighted so far are illustrated in Figure 1.3. Figure 1.4 compares a recent theoretical phase portrait to an experimentally obtained one for poly(styrene)-b-poly(isoprene) diblocks. The comparison is quite favorable in terms of observed phases and their locations. Both diagrams show the classical morphologies (LAM, HEXC, and BCC) with an additional channel in between LAM and HEXC where the gyroid phase is predicted to be most stable.

In some respects, the sphere-forming region of block polymer self-assembly is the most interesting as it bears connections to other, seemingly unrelated, classes of
materials. The sphere-packing problem can be examined in two limits. In the first case, packing of hard-spheres is purely dominated by entropy and adopts a close packed solution of face-centered cubic (FCC) or hexagonal close-packing (HCP). The second case, which addresses the packing of equal-size bubbles, is purely an interfacial issue. Weaire and Phelan proved the optimal solution to this problem was the A15 lattice (examined in more detail in section 1.2.4). The self-assembly of block copolymers is governed by a delicate balance of both entropic and enthalpic contributions, leading to a richness in sphere-forming phase behavior which extends far beyond these limiting cases. Though the BCC phase was thought to be synonymous with sphere-forming phase behavior, experiments on short \( M_n = 2-5 \text{ kDa} \) poly(isoprene)-b-poly(lactide) (IL) diblock polymers where L forms the spherical core have revealed the presence of a Frank-Kasper \( \sigma \) phase (\( \sigma \)) and quasicrystalline order (DDQC). Continued investigation of these materials has revealed captivating parallels between self-assembly in soft and hard materials. For example, Lee et al. have drawn unanticipated analogies between symmetry breaking in diblock copolymers, mediated by mass exchange, and symmetry breaking in metals and alloys, mediated by exchange of charge. Additionally, Gillard et al. contextualized the formation of BCC, \( \sigma \), and the DDQC phases by mapping structure formation onto a time-temperature transformation diagram similar to those seen in the materials science literature. Additional factors influencing diblock phase behavior, such as the role of conformational asymmetry and chirality, continue to be researched.

1.2.2 Triblocks

ABA triblocks. A symmetric ABA triblock is the simplest extension of the AB diblock architecture. In an ABA copolymer, both ends of the B block are pinned to an interface allowing the formation of two distinct configurations (Figure 1.5). In the bridging configuration, the two A blocks are distributed in two different A domains while in the looping configuration, both A blocks are confined to the same domain. Though this has little effect on phase behavior, the triblock architecture has been shown to greatly improve mechanical properties due to the presence of bridging chains. In addition, an
ABA architecture also allows the introduction of a symmetry parameter $\tau$ ($0 \leq \tau \leq 0.5$) such that the shorter A block has $\tau f_A N$ segments and the longer A block has $(1 - \tau)f_A N$ segments.

The phase behavior of ABA triblocks was first addressed by Helfand and Wasserman who found the domain sizes for these two architectures different only by a few percent and exhibit nearly identical phase behavior at strong segregation. Experiments confirmed these predictions by identifying the same BCC, LAM, HEXC, and GYR phases in triblock melts. The work of Cruz et al. predicted that a symmetric ABA triblock would exhibit a critical point at $f_A = 0.5$ and $(\chi N)_{ODT} = 17.9$, rather than 10.5, as in the diblock case; this was verified by several experimental groups. Matsen and co-workers again computed phase diagrams using SCFT for the case of a symmetric ABA triblock as shown in Figure 1.6. They found homologous diblock melts (such that $N = 2N_{AB} = N_{ABA}$) disorder at a higher $\chi N$ since the end A segment only has to drag half as much B segment into the A domain. Accordingly, this discrepancy was much more pronounced on the large $f_A$ side of the phase diagram where disorder results due to B blocks releasing from their domains. The slightly higher segregation also caused interfacial widths to be narrower in the ABA case. Examination of asymmetric ABA triblocks revealed that small asymmetries ($\tau \approx 0.5$) induced a slight increase in the domain spacing and a shift of order-order transitions to higher $f_A$. Larger asymmetries allowed A chains to pull free of their domains significantly increasing domain spacings.
1.2 Block polymer phase behavior

Figure 1.6 SCFT calculated mean-field phase diagrams for an AB diblock copolymer (dashed curve) overlaid on one for a symmetric ABA triblock copolymer (solid curve) highlighting the difference in $(\chi N)_{\text{DOT}}$ and asymmetry in phase behavior. Note that $N = 2N_{\text{AB}} = N_{\text{ABA}}$. Adapted from Matsen, M.W., *J. Chem. Phys.*, 113, 5539-5544 with the permission of AIP publishing.

ABC triblocks. Introducing a third monomer into a triblock architecture significantly amplifies the number of variables that govern phase behavior. While mean field diblock phase behavior can be summarized by $\chi_{\text{AB}}N$ and $f_A$, at least five independent parameters are required to map ABC triblock phase behavior ($\chi_{\text{AB}}N, \chi_{\text{AC}}N, \chi_{\text{BC}}N, f_A,$ and $f_B$). Since the relative values of each interaction parameter influence the phase behavior considerably, changing both the chemistry or block sequencing (ABC vs. ACB) can alter the observed morphologies. Thus, a comprehensive theory capturing ABC phase behavior is extremely challenging. Exploring such a daunting parameter space has required the concurrent theoretical\textsuperscript{105–111} and experimental\textsuperscript{112–129} efforts of several groups. Here, we place emphasis on highlighting the work of Bailey et al.\textsuperscript{130} who worked with triblock terpolymers of poly(styrene), poly(isoprene), and poly(ethylene oxide), the same monomers that are utilized in this thesis. In order to establish some universality in this large parameter space, Bailey proposed a categorization scheme based on the relative values of the Flory-Huggins interaction parameters, $\chi_{\text{AB}}, \chi_{\text{AC}},$ and $\chi_{\text{BC}}$.

An ABC architecture mandates the formation of two interfaces: A/B and B/C. However, the third A/C interface is formed only when energetically favorable. Recognizing this, Bailey proposed three classes for ABC systems: (1) $\chi_{\text{AB}} \leq \chi_{\text{BC}} \leq \chi_{\text{AC}}$:
the A/B and B/C interfaces are most favorable and the system possesses no drive to favor formation of A/C interfaces. Such a system is called non-frustrated (F₀). (2) \( \chi_{AB} \leq \chi_{AC} \leq \chi_{BC} \): the A/C interaction is more favorable than only the B/C interaction and this system is defined as possessing type I frustration (F₁). (3) \( \chi_{AC} \leq \chi_{AB} \leq \chi_{BC} \): the mandatory A/B and B/C interfaces are energetically least preferred driving the formation of A/C interfaces. This system exhibits type II frustration (F₂). Bailey provided a comprehensive summary of the phase behavior differences resulting from each type of frustration (F₀, F₁, or F₂).¹³⁰

Systematic studies of triblocks containing poly(styrene) (S), poly(isoprene) (I), and poly(ethylene oxide) (O) were undertaken to elucidate the phase behavior differences arising from the frustration condition. SIO (F₁) and ISO (F₀) triblock terpolymers were synthesized using a two-step anionic polymerization method. The synthetic procedure allowed the reinitiation of an AB diblock in order to synthesize the corresponding ABC triblock, facilitating the generation of multiple triblocks samples from an initial stock of AB precursor.¹³¹,¹³² This assured that all samples lay on precisely the same \( f_S = f_I \) isopleth and differed only in the amount of O. As these triblocks were characterized between \( 0 \leq f_O \leq 0.33 \), the frustration condition was shown to have a profound impact on phase behavior. Four morphologies were observed between the 2-domain (\( f_O \approx 0 \)) and 3-domain (\( f_O \approx 0.3 \)) lamellar phases in SIO: a pillared lamellar structure (PLS), hexagonally packed core-shell cylinders (CSC), penta-continuous core-shell gyroid (CSG), and semi-perforated lamellae (SPL). Both PLS and SPL morphologies formed A/C interfaces which illustrated the importance of frustration in determining phase behavior.¹³¹ In contrast, only one morphology was reported between the 2- and 3-domain lamellae in ISO: a non-cubic, triply periodic network phase called O⁷⁰ (space group \( F_{ddd} \)).¹³² The same structure was later identified in poly(cyclohexylethylene)-\( b \)-poly(ethylene)-\( b \)-poly(dimethylsiloxane) (CED)¹³⁴ samples, indicating a degree of universality to this morphology. Motivated by the prevailing interest in exploring network forming phases, further synthetic and characterization efforts focused on examining the ISO system along other \( f_S/f_I \) isopleths and led to the discovery of the BCC morphology and two additional
network phases, Q\textsuperscript{230} and Q\textsuperscript{214}.\textsuperscript{135–138} A fourth network phase, termed O\textsuperscript{52}, was also observed in CEE triblocks, but only through a shear-induced phase transition.\textsuperscript{133}

1.2.3 Tetrablocks

The move to a tetrablock architecture is a practical example of the enormous complexity involved with fully exploring block polymer phase behavior.\textsuperscript{11} Even a relatively simple tetrablock ($n = 4$) composed of only three different chemistries ($k = 3$) has nine different enumerations of block sequences (ABAC, ABCA, ACAB, ACBC etc.). Increasing the number of blocks and chemistries is accompanied by a rapid escalation in the enumeration possibilities (e.g. $n = 5$ and $k = 4$ leads to 72 unique options).

Preliminary studies of ABCA-type poly(ethylene oxide)-$b$-poly(styrene)-$b$-poly(butadiene)-$b$-poly(ethylene oxide) (OSBO) tetrablocks with equal sized O blocks by Brannan et al. have yielded a host of decorated lamellar morphologies.\textsuperscript{139} The synthetic strategies outlined in chapter 3 allow the generation of OSBO′ tetrablocks where the corona chains can be of varying length, expanding phase behavior possibilities.\textsuperscript{11} In fact, such ABCA′-type tetrablocks have already been shown to produce non-centrosymmetric lamellar structures (with sequence ...ABCABCABC...) by Takano et al.\textsuperscript{140}

Initial exploration of a ABAC-type tetrablock architecture was driven by interest in further expanding the variety of network phases. It was postulated that breaking the molecular symmetry of an ABC triblock to produce the corresponding ABAC tetrablock would yield new phase behavior. These predictions proved correct when varying the CED triblock to a CECD molecular architecture produced the O\textsuperscript{52} network structure. Motivated by these findings, Bluemle et al. explored similar possibilities by synthesizing poly(styrene)-$b$-poly(isoprene)-$b$-poly(styrene)-$b$-poly(ethylene oxide) (SISO) tetrablock terpolymers.\textsuperscript{141} However, the phase behavior discovered here was unexpectedly different with a propensity for yielding core-shell spheres ($0.04 \leq f_0 \leq 0.09$) and cylinders ($f_0 \geq 0.12$). Initial experiments found the spherical domains displayed only liquid-like packing.\textsuperscript{141} However, further experiments revealed that the $f_0 = 0.08$ sample formed the $\sigma$ phase at elevated temperatures.\textsuperscript{93} Exploration of these fascinating polymers along other $f_S/f_I$ isopleths has yielded exotic morphologies such as a dodecagonal quasicrystal\textsuperscript{142} and
1.3 Frank-Kasper phases and Quasicrystals

The discovery of complex Frank-Kasper phases and quasicrystalline order in sphere forming block copolymers is quite recent. Therefore, a short introduction to the fascinating history and fundamental properties of these morphologies is provided here.

**Frank-Kasper Phases.** In 1952, Sir Frederick Charles Frank posed the following question: “In how many different ways can one put twelve billiard balls in simultaneous contact with one…” There are three distinct arrangements that can accommodate this constraint: hexagonal-close packing, face-centered cubic, and an icosahedron. Frank demonstrated that the 12-fold icosahedral coordination yielded a lower total energy than the HCP and FCC arrangements of the same 13 atoms when interacting through a Lennard-Jones potential. The conclusion followed from geometrical considerations; the distance from the central to vertex atoms in an icosahedral arrangement is shorter than the other two possibilities and able to accommodate densely packed liquids. Additionally, the spheres of the shell are not in contact with each other, allowing a freedom of deformation which can accommodate coordination requirements of atoms other than the central one. Structural stability of the icosahedral unit was used to elucidate reasons behind the formation of many complex alloy structures and predict hypothetical crystalline structures (many of which have been confirmed in subsequent years).

However, the limitation of trying to form crystalline structures which tessellate 3D space from icosahedral units is immediately clear. Icosahedra (point group m35) cannot fill space completely without gaps. Frank and Kasper postulated three additional polyhedra, CN14, CN15, and CN16 (Figure 1.7a) which were used in tandem with the icosahedral unit (CN12) to tile space in a crystalline manner. Since all these polyhedra have exclusively tetrahedral interstices, all Frank-Kasper phases are known as tetrahedrally or topologically close-packed (TCP) structures. In contrast, close packed structures such as FCC and HCP contain octahedral interstices that cannot pack as
1.3 Frank-Kasper phases and Quasicrystals

Figure 1.7 (a) Illustrations of the Frank-Kasper coordination polyhedra. Combinations of these units are used to tessellate 3D space in a periodic manner in all Frank-Kasper phases. (b) Frank-Kasper A15 phase built up with CN12 and CN14 coordination polyhedra. (c) Frank-Kasper σ phase built by using CN12, CN14, and CN15 polyhedra. Note that the two different shades of red (CN12) and blue (CN14) are used to signify sites that share the same coordination polyhedra but different Wyckoff positions.

Densely as TCP. In fact, a tetrahedron is the densest possible method of packing 4 isolated, equal spheres. However, since tetrahedra cannot tessellate three dimensional space, slight deformations are required within the four Frank-Kasper polyhedra to enable translational periodicity. Regardless, the common feature of TCP polyhedra in Frank-Kasper phases highlights their importance as efficiently packed local units and rationalizes their stability in a variety of soft materials and densely packed liquids which can accommodate the required deformations.

Two Frank-Kasper phases of particular importance in this work are A15 and σ phase. The A15 structure (space group Pm\(\overline{3}\)n) contains 8 spheres in each unit cell and is the most prevalent Frank-Kasper phase in soft materials.\(^8^4\) It has an A\(3\)B stoichiometry with A sites embedded in the 14-fold coordination polyhedra and B sites in 12-fold icosahedral coordination (Figure 1.7b).\(^1^4^7\) The Frank-Kasper σ phase, with a giant unit
Figure 1.8 1D illustration of the strip/projection method. First, a cut of the 2D lattice at an irrational slope ($\tau=(1+\sqrt{5})/2$) is taken. This is followed by a projection of sites of the 2D lattice inside the strip (yellow). The result is an aperiodic but ordered arrangement of L (green) and S (red) segments mimicking the Fibonacci chain.

cell containing 30 spheres, is a testament to the fascinating complexity block polymer self-assembly can display. The 30 spheres are split among five different sites $M(1)$, $M(2)$, $M(3)$, $M(4)$, and $M(5)$. The coordination polyhedra around $M(1)$ and $M(4)$ are CN12, around $M(3)$ and $M(5)$ are CN14, and around $M(2)$ is CN15 (Figure 1.7c). As discussed in section 1.2.1, the $\sigma$-phase has been encountered in close proximity to quasicrystalline order in diblock polymers.

Quasicrystals. It is quite straightforward to show from geometric considerations that structures possessing 5-fold rotational symmetry (e.g. regular pentagons) cannot tile a two dimensional plane without leaving gaps. In fact, periodicity in two or three dimensions was thought to require structures that are 2-, 3-, 4-, or 6-fold rotationally symmetric. This view was challenged in 1984 by Dan Shechtman who found icosahedral symmetry (including 5-fold rotational axes) in a rapidly solidified Al-Mn alloy. This was followed by the discovery of 8-, 10-, and 12-fold rotationally symmetric structures in different metallic alloys. Materials such as these, called quasicrystals, are characterized by discrete diffraction peaks indicating long range order but with observed rotational symmetries that are inconsistent with periodicity.

The aperiodicity observed in quasicrystals still preserves orientational order (i.e., placement of atoms or micelles is not random). This concept can be simplified and illustrated through the strip/projection method shown in Figure 1.8. The figure displays
Figure 1.9 Structural model of the dodecagonal quasicrystal using Frank-Kasper A15 and σ approximants. These phases are generated by tessellation of squares and triangle tiles containing particles at particular positions along the z-axis. (a) The cubic A15 phase tiling requires only square tiles while (b) the tetragonal σ phase requires the same squares and two distinct equilateral triangles. (c) An aperiodic arrangement of the same three tiles can be used to generate a structural model of the DDQC. Adapted from Ungar, G. and Zeng, X., Soft Matter, 1, 95-106 with permission of the Royal Society of Chemistry.84

a periodic 2D square lattice in which a 1D line of slope τ (the golden mean) is embedded. Since this slope τ is irrational, the line cannot intersect the 2D lattice at any point. Sites of the 2D lattice within a pre-defined strip are projected on the line yielding a structure made of two tiles (L and S). This projection is referred to as an “incommensurate” projection due to the irrational slope involved. Distribution of the obtained L and S segments follows the Fibonacci chain and is, therefore, mathematically ordered but clearly aperiodic (a repeating structure of the L and S segments cannot be found at any length scale). While this example illustrates a cut-and-project procedure from an ordered 2D lattice to a 1D space, similar procedures can be used to describe quasicrystalline materials. For example, an incommensurate 2D projection from a 5D periodic structure has been shown to yield the well-known Penrose tiling.151 Similar projections from 6D space yield the previously mentioned icosahedral quasicrystals first reported by Shechtman et al.148

Different types of quasicrystals have been documented in intermetallic alloys,148 soft matter,84 and even natural minerals.152 In this work, a 2D dodecagonal quasicrystal (DDQC), characterized by periodicity parallel to the 12-fold axis, is reported. One possible structural model of the DDQC in the xy plane is shown in Figure 1.9. In this model, the relationship between the DDQC and aforementioned A15 and σ phases is
clear; quasicrystalline order is generated by aperiodic tiling of the same square and triangle tiles used to generate the periodic Frank-Kasper phases. These tiles are decorated with particles at certain elevations and are periodic in the $z$ direction. Since the A15 and $\sigma$ phases contain motifs observed aperiodically in the DDQC, they are known as periodic approximants. It is worth noting that other structural models of the DDQC exist and reveal other approximants. Since the DDQC is an incommensurate projection of a 5D periodic structure, five independent basis vectors are needed to describe the scattering patterns. This work follows the scheme used to index DDQC scattering patterns described by Ishimasa et al. and Gillard et al.

### 1.4 Overview

This thesis details the synthesis and structural characterization of a variety of tetrablock terpolymers using differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMS), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). The model materials chosen for these studies involve tetrablocks containing poly(styrene), poly(isoprene), and poly(ethylene oxide). The overarching goal of the thesis is to expand on the work done previously on the SISO system, while exploring new molecular architectures (ISIO) and introducing additional synthetic strategies.

Chapter 2 outlines the basics and methodology of the experimental and theoretical methods used to elucidate tetrablock terpolymer morphologies in this work. New synthetic strategies for the production of ABCA'-type tetrablock terpolymers are presented in Chapter 3. Chapter 4 addresses the influence of varying the molecular symmetry parameter, $\tau = N_A/(N_A + N_A')$, on the phase behavior of ABA'C-type polymer taking SIS'O as the model system. The phase behavior of this system is further studied in chapter 5 with the specific goal of exploring the unresolved structure of the HEX$_5$ phase in low $\tau$ systems. Finally, chapter 6 examines the effect of introducing the frustration condition to a tetrablock architecture by studying phase behavior differences which arise when transitioning from a SISO to an ISIO tetrablock terpolymer.
Chapter 2

Methods

Characterization of block polymer phase behavior is predicated on the synthesis of well-defined materials with low dispersity and required volume fractions. The following sections detail anionic polymerization protocols used to synthesize ABAC-type tetrablock terpolymers (the synthesis and characterization of ABCA’-type polymers are the subject of chapter 3). The molecular characterization of the resultant polymers is accomplished through size exclusion chromatography (SEC) and $^1$H nuclear magnetic resonance spectroscopy ($^1$H NMR). Thermal and morphological characterization uses differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). These techniques are described briefly in the following chapter.

2.1 Polymer synthesis

The synthesis of ABAC-type tetrablocks is achieved by exclusively using anionic polymerization, a chain-growth technique which avoids undesirable chain transfer and termination steps. Basic principles underlying this technique along with description of the materials and strategy employed are described in the next few sections.
2.1 Polymer synthesis

2.1.1 General aspects

Polymerization schemes that contain no irreversible chain transfer and termination reactions have been termed “living” polymerizations. This technique was first demonstrated by Szwarc in 1956 who successfully polymerized styrene and isoprene via electron transfer of sodium naphthelanide to styrene. The reaction consists of four steps: dissociation of the initiator, initiation via nucleophilic attack, propagation by transfer of the active carbanion site to another monomer, and termination. Details pertaining to the kinetic scheme can be found elsewhere. However, it is important to note that the distribution describing the mole fraction, $x_i$, of an $i$-mer (i.e. a polymer with $i$ repeat units) among all polymer chains is:

$$x_i = \frac{\bar{p}^{i-1}e^{-\bar{p}}}{(i-1)!}$$  \hspace{1cm} (2.1)

where $\bar{p}$ is the ratio of the number of monomers incorporated into polymers to the number of polymers. This function is called the Poisson distribution and describes the situation whenever a large number of objects is distributed randomly among a small number of recipients. The kinetics of anionic polymerization follows the Poisson distribution when the following requirements are satisfied: i) chain transfer and termination steps are absent, ii) all active chain ends are equally likely to react, iii) all active chain ends are introduced at the same time, and iv) propagation is essentially irreversible. If the reaction is allowed to go completion, the number average molecular weight, $M_n$, can be controlled simply by adjusting the ratio of moles of monomer used to the moles of initiator added. Additionally, the distribution of chain lengths can be computed resulting in the following expression for dispersity ($D$):

$$D = \frac{M_w}{M_n} = 1 + \frac{N_n}{(1 + N_n)^2} \approx 1 + \frac{1}{N_n}$$  \hspace{1cm} (2.2)

This expression demonstrates an important advantage of using anionic polymerization; the dispersity attained is usually much less than 1.10 for any practical $N_n$. This is important in the characterization of block polymer phase behavior because of the implicit assumption that these materials are pure and nominally one-component. Both
experiments$^{156,157}$ and simulations$^{158-160}$ have confirmed that increasing dispersity can impact the equilibrium morphology and domain spacing if $D > 1.10$.

Despite these strengths, anionic polymerization does have a few limitations.$^1$ For example, monomers are limited to those that have double bonds (vinyl, diene, or carbonyl) and heterocyclic rings. In vinyl monomers (CH$_2$=CHX), the X group must have some electron withdrawing character in order to stabilize the active carbanion end. For anionic ring opening polymerization, the ring must be amenable to nucleophilic attack and result in a stable anion. Functionalities containing an acidic proton (e.g. -OH) or an electrophilic functional group (e.g. O$_2$, CO$_2$) will interfere with the anionic mechanism and must be protected if the reaction is to proceed. As a consequence, the reaction vessel must also be rigorously pure of any impurities, especially water, oxygen, and carbon dioxide.

Reactivity of the chosen initiator must be comparable or slightly higher than the reactivity of the resulting carbanion. As expected, lower initiator reactivity prevents the reaction from proceeding but extremely high reactivity can result in unwanted side reactions. Common initiator classes include alkali metals, radical anions, and alkyllithiums. The latter two will be used in the synthetic strategy presented here. A good solvent will dissolve both the initiator and monomer species as well as be inert to carbanions. Additionally, the choice of solvent influences the microstructure of the resulting polymer. For example, anionic polymerization of polyisoprene in a polar solvent favors 3,4- and 1,2-addition while switching to a nonpolar solvent favors the 1,4-cis microstructure. Initiator choice and concentration can also influence the microstructure of the resulting polymer.$^1$ Nonpolar solvents tend to cause ion pairing or clustering of the active ends due to the low solubility of ionic species in hydrocarbons. Tight association between the anion and counterion forms dipoles which associate into small clusters of two to six chains. Thus, an additional dissociation step is required before the growing end can react leading to slower propagation kinetics in nonpolar solvents. Termination of the growing ends can be attained quite easily with the introduction of an acidic proton source. However, care must be taken to avoid the introduction of any
impurities in this final step. For example, introduction of oxygen can lead to the formation of dimers due to coupling of two living chains.

Finally, anionic polymerization allows sequential addition of monomers in order to allow the facile synthesis of block copolymers with a minimum number of intermediate steps. For example, Funabashi et al. were able to synthesize pentablock terpolymers of ABACA-type using five-stage sequential addition with no intermediate purification or end group modification required.\textsuperscript{161} However, this strategy has some limitations which can be circumvented by appropriate choice of monomers. Sequential addition means one block is polymerized to completion but not terminated; the next monomer can simply be added to the same reaction mixture. The preceding block serves as a macroinitiator for the following synthesis. There are a few requirements for this strategy to be employed. Firstly, the carbanion of the first block must be able to initiate the second block. This requires the stability of the second block carbanion to be equal or greater than that of the first block. For example, the poly(2-vinylpyridine) (V) carbanion is more stable than that of poly(styrene) (S). Therefore, anionic polymerization can produce a SV diblock but not a SVS triblock.\textsuperscript{162} Secondly, the solvent system must be suitable for all blocks and, lastly, the counterion must also be appropriate for the polymerization of each block. Though all these restrictions seem limiting at first, creative use of synthetic strategies has allowed the creation of almost any architecture with a variety of monomers. In addition to sequential addition, coupling chemistry\textsuperscript{140} and reinitiation of telechelic blocks\textsuperscript{163} are important parts of the growing synthetic toolkit for producing block polymers.

\subsection*{2.1.2 Materials}

Maintaining a high purity environment is essential to a successful anionic synthesis and requires strict purification procedures. The following paragraphs detail the materials used along with relevant purification procedures.

\textbf{CAUTION}: The following sections describe the use of extremely hazardous classes of chemicals. The handling of these reagents presents many hazards and must only be performed by properly trained researchers following established standard operating procedures while using appropriate personal protective equipment and engineering
controls. Extreme caution must be exercised when handling pyrophoric metals and organometallics as they cannot be exposed to ambient humidity or air. Ethylene oxide (EO) is particularly hazardous as it is flammable, toxic, carcinogenic, highly reactive, and extremely volatile (BP = 10.7 °C). This monomer should not be allowed to warm up, especially when stored in a sealed container, in order to avoid an explosion.

**Solvents.** Cyclohexane solvent was degassed by sparging with argon and stored under pressurized argon. The solvent was then passed through two columns packed with activated alumina (A15 grade) and an oxygen scavenging copper catalyst (CU-0226S, Engelhard) in a custom built solvent purification system. Tetrahydrofuran (THF) was also degassed by sparging with argon. THF was then passed through two columns packed with activated alumina. The copper-alumina redox catalyst is not utilized in this case due to side-reactions with the THF ether group. In cases where greater purity was required, the THF was exposed to sec-BuLi or a sodium/benzophenone ketyl still pot.

**Purification agents.** Dibutylmagnesium (diBuMg, 1M solution in heptane, Aldrich) and n-butyllithium (n-BuLi, 2.5M solution in hexanes, Aldrich) were dried under reduced pressure (<100 mTorr) prior to use. Argon gas (high purity grade) was purified by passing through a OMI-2 purifier tube upstream of Schlenk line.

**Initiator.** The two initiators used in this study were sec-butyllithium (sec-BuLi) and potassium naphthalanide (KNaph). The sec-BuLi was used as received. However, it was titrated using established procedure to ascertain the solution concentration before anionic synthesis. Briefly, n-benzylbenzamide (>98%, Aldrich) was dried overnight under high vacuum and tetrahydrofuran (THF) was purified using a sodium/benzophenone ketyl pot. Dried n-benzylbenzamide was dissolved in the purified THF. The sec-BuLi solution was added dropwise to the solution at -40 °C until the endpoint is reached (indicated by a persistent dark blue color). This procedure yields concentrations very similar to the Gilman double titration method using a much simpler experimental procedure.

KNaph was synthesized by reaction of potassium metal and naphthalene in THF. Approximately 0.5 g of potassium (chunks in mineral oil, >98%) were first placed in hexanes to dissolve residual oils. The metal was then transferred to a flask with a 24/40
port under dynamic argon. Care must be taken to minimize exposure of the pyrophoric metal to air and water. The hexanes were evacuated by vacuum and approximately 200 mL THF from the solvent purification system was introduced to the flask. After addition of a 10% molar excess of naphthalene, the solution was left to stir and react overnight.

**Monomers.** The monomers utilized in this work are styrene, isoprene, and ethylene oxide. Styrene (99%, 10-15 ppm p-tert-butylcatechol inhibitor, Aldrich) was freeze-pump-thawed at least three times. Freezing the monomer reduces the solubility of any dissolved gases which are then evacuated by vacuum. This process is repeated until the vacuum reading does not increase appreciably above baseline. The styrene is purified further by two distillations over dried dibutylmagnesium at 40 °C for one hour each. Approximately 0.5 mL of the dibutylmagnesium solution were used to purify every 5 g of styrene (0.1 mmol diBuMg/g styrene). The styrene is collected in a single ended burette, backfilled with pressurized argon, and mounted on the reactor. The burette is covered with aluminum foil to prevent photo polymerization. Isoprene (99%, 100 ppm p-tert-butylcatechol inhibitor, Aldrich) was also purified in a similar manner starting with a sufficient number of freeze-pump-thaw cycles. It is then distilled over dried n-butyllithium twice at 0 °C for 30 minutes each using a concentration of 0.25 mmol n-BuLi/g isoprene. Finally, the isoprene is collected in a single ended burette, backfilled with pressurized argon, and attached to the reactor. Ethylene oxide (99.5%, compressed gas, Sigma-Aldrich) is collected in a flame dried flask, freeze-pump-thawed thrice and distilled twice over n-butyllithium (0.25 mmol n-BuLi/g ethylene oxide). Due to the volatility of ethylene oxide, all purifications are carried out for 30 minutes each using a cooling ice bath containing salt. Additionally, the highly strained nature of ethylene oxide ring may warrant a milder purification agent; butylmagnesium chloride should be considered as an alternative in the future.

### 2.1.3 Synthetic strategy

**Synthesis of ABA-OH triblock.** Here, the technique to synthesize hydroxyl end-capped poly(styrene)-b-poly(isoprene)-b-poly(styrene) (SIS-OH) or poly(isoprene)-b-poly(styrene)-b-poly(isoprene) (ISI-OH) is presented. The experimental setup and steps
for the synthesis of both triblocks are nearly identical; the only difference is the sequence in which monomers are introduced. Thus, the following will outline the synthesis of SIS-OH triblocks. Custom-made, modular glassware is used throughout. A 3L spherical glass reactor with 6 ports (size 5, Ace glass) is used to synthesize 40 g of SIS-OH triblock. Attachments to the reactor include: i) an airlock so that ethylene oxide can be introduced to the reactor, ii) a solvent flask containing 1 L cyclohexane, and iii) a three-port manifold which connects to vacuum/argon Schlenk line, a pressure gauge, and allows small withdrawals from or additions to the reaction solution. The remaining ports are fitted with single-ended burettes containing purified styrene and isoprene monomers. A teflon stir bar is inserted to ensure the reaction solution is well-mixed. All glassware have ½" OD tubing which can be attached to the reactor ports using Teflon ferrules (Ace glass) and nylon bushings (Ace glass). After assembly, the reactor is left to evacuate under high vacuum (<100 mTorr) overnight. If the reactor is able to reach and sustain baseline pressure (indicating no leaks), six vacuum/argon cycles are performed to remove air. The reactor is flamed thrice under vacuum to remove residual water. Polymerization reactions were performed after the reactor was sealed at 3-4 psig of argon pressure.

In a typical reaction, approximately 1L of cyclohexane is added to the dried reactor and heated to 40 °C using a temperature controlled water bath. The correct volume of sec-BuLi needed (as determined by initiator titration and target molecular weight) is collected in a gas tight syringe fitted with a 12-inch needle while working within the glove box. A small molar excess (10%) of the initiator is withdrawn and introduced to the solvent. This excess reacts with any remaining protic impurities within the reactor preventing unwanted chain termination after the monomer is introduced. After 10 minutes, styrene monomer is introduced to the reactor and allowed to react for no more than 8 hours. Before introduction of the second monomer, a small aliquot is collected for size exclusion chromatography. To collect the aliquot, a clean cannula is inserted into the reactor under dynamic argon and allowed to purge for a minute. The cannula is then submerged in the reaction solution to allow the poly(styrene) solution to flow into a flask containing degassed methanol. After retrieving the aliquot, the reaction is allowed to
2.1 Polymer synthesis

Figure 2.1 SISO tetrablock synthesis scheme.

Proceed for another five to eight hours. Another aliquot is collected before addition of the final monomer. While the reaction proceeds, a ten-fold molar excess of ethylene oxide (~1g) is purified and collected in a burette. The EO burette is connected to the airlock using a ½” OD flex tube. EO is then introduced to the reactor resulting in the incorporation of a single EO unit. In small amounts, EO does not cause an appreciable pressure increase. However, additions should be handled safely when working with larger quantities by submerging the EO burette in ice water if the reactor pressure exceeds 6 psig. After four hours, the reaction is terminated with degassed methanol yielding the final SIS-OH or ISI-OH triblock copolymers. The reactor is opened and allowed to vent excess EO overnight. The reaction solution is then precipitated in 4L of cold (4 °C) methanol. The precipitate is allowed to settle overnight and the methanol is separated using a sintered glass filter. Residual solvents are eliminated by freeze-drying the remaining white powder from benzene.

Synthesis of ABAC-OH tetrablock. The reinitiation of ABA-OH to produce the corresponding ABAC-OH tetrablocks is quite advantageous as it allows the synthesis of
several tetrablocks using a single triblock precursor. This ensures that the poly(styrene) and poly(isoprene) volume fraction ratio does not change within the whole series of ABAC tetrablocks. The reaction scheme for producing SISO tetrablocks is illustrated in Figure 2.1. A small 1L reactor with 5 ports is filled with a glass stir bar and approximately 3.0g of triblock precursor. It is then fitted with an airlock, the reaction manifold, and a smaller solvent flask containing about 100 mL of THF. The remaining ports are sealed with glass plugs. The reactor is left to evacuate overnight under dynamic vacuum (<100 mTorr); reaching a sustained baseline reading assures the reactor is free of leaks. The reactor is exposed to six cycles of pressurized argon and high vacuum to remove air. The assembly is not flame-dried this time in order to prevent accidental degradation of the polymer. Once the reactor is dry, THF is added and allowed to dissolve the triblock. Complete dissolution is important as undissolved chains will not undergo reinitiation and subsequent polymerization. KNaph is then transferred to the reactor by use of cannula or a syringe fitted with a dried 12-inch needle. The titration solution is added until a pale green color can be sustained for at least 30 minutes. After the endpoint is reached, the solution is heated to 40 °C and excess pressure is released through the manifold. Purified EO is then attached to the airlock using a ½’’ OD flex tube and introduced to the reactor. The reaction is allowed to proceed for 24h and terminated with degassed methanol. After the solution stirs for an hour, the reactor is opened to allow EO to vent overnight. The resulting polymer can be separated from the solution using rotary evaporation followed by precipitation in cold (-78 °C) methanol or liquid-liquid extraction (described in further detail in chapter 4 and chapter 6, respectively). Both purification methods seldom produce a yield better than 60% due to the amphiphilic nature of the tetrablock terpolymers. However, precipitation is the preferred method as it consistently obtains a higher yield and is much less time consuming. The purified polymer is dissolved in a minimal volume of benzene along with 0.5 wt% butylated hydroxytoluene which prevents polymer degradation. The solution is freeze-dried overnight to obtain the final SISO or ISIO tetrablock sample.
2.2 Size exclusion chromatography

Depending on the calibration or detection scheme used, size exclusion chromatography (SEC) can yield information on a sample's molecular weight, molecular weight distribution, chemical composition, or even architecture. In addition, SEC has rapid sample throughput (~45 min) and is easily automated making it a very powerful characterization technique. In this study, SEC is utilized to attain molecular weights and molecular weight distributions in order to quantify the quality of synthesized tetrablocks. The basic separation process relies on a series of columns, each packed with a material of different characteristic porosity (stationary phase). A small amount of dilute (1 mg/mL solvent) polymer solution (mobile phase) is injected into the machine upstream of the column. Compatibility between the packing material, solvent, and polymer is extremely important to avoid undesirable interactions which lead to erroneous data or column damage. The solution flows slowly (1 mL/min) but steadily through the column with the aid of a high quality pump. As the polymer solution passes through the porous columns, chains of lower hydrodynamic volumes ($V_h$) explore more of the porous structure and elute at a later time. Conversely, samples with a higher $V_h$ are unable to pass through the smallest pores and elute earlier. Thus, the separation mechanism for SEC is based on size, not molecular weight. A suitable detector monitors the eluting solution and records its concentration as a function of the volume of solvent that passes through the column before a polymer of a particular $M$ is eluted (called the retention volume, $V_R$). Refractive index or UV-Vis detectors are most commonly used and can be combined with light scattering detectors to obtain absolute $M_w$. Representative data is shown in Figure 2.2.

$V_R$ must be related to $M$ through suitable calibration strategies. The first direct calibration strategy uses a series of polymers of known $M$, known as calibration standards. Running these through the SEC column generates a curve of log$M$ vs $V_R$ which can be used to assign a value of $M$ to all subsequent samples. However, the limitation here is clear: separation is based on $V_h$, and not $M$ directly. Thus, accuracy in $M$ requires the use of standards of the same polymer as the analyte; this is especially problematic for block polymers as frequently calibration standards simply do not exist. The second
2.2 Size exclusion chromatography

Figure 2.2 Representative SEC data from sequential anionic polymerization of poly(styrene) (S) and a poly(styrene)-b-poly(isoprene) (SI) diblock. The transition to a lower retention time indicates successful growth of the I block. Qualitatively, elution peaks seem narrow and symmetric indicative of monodisperse polymers but a small fraction of terminated chains is clearly visible.

strategy is known as universal calibration and relies on the idea that, regardless of detailed molecular structure

\[ \eta \sim \frac{V_h}{M} \approx \frac{R_g^3}{M} \]  

(2.3)

where \([\eta]\) is the intrinsic viscosity and \(R_g\) is the radius of gyration. Thus, the \(V_h\) should be proportional to \([\eta]M\). Combining this with the Mark-Houwink relation (\([\eta] = kM^a\)), we find the following relation is valid at each slice of \(V_R\):

\[ ([\eta]M)_c = k_c M_c^{1+a_c} = ([\eta]M)_u = k_u M_u^{1+a_u} \]  

(2.4)

\[ M_u = \left( \frac{k_c M_c^{1+a_c}}{k_u} \right)^{1/(1+a_u)} \]  

(2.5)

where \(c\) and \(u\) refer to calibration standard and unknown sample, respectively. If the Mark-Houwink parameters are known, this equation can be used to obtain \(M\) of the unknown polymer with respect to the calibration standard at any \(V_R\). As discussed in chapter 6, this universal calibration strategy was combined with data from \(^1H\) NMR in order to calculate the molecular weights for ISIO tetrablocks. Direct calibration data is also combined with \(^1H\) NMR experiments in order to calculate the molecular weights for
SISO sample as detailed in chapter 4. More importantly, the dispersity and molecular weight distributions of all samples and intermediate aliquots can be monitored using the SEC traces, providing valuable insight into the quality of the synthetic procedure.

2.3 Proton nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is an analytical technique used frequently in organic chemistry to elucidate chemical structures. Nuclei that have a magnetic moment such as $^1$H, $^{13}$C, $^{15}$N or $^{19}$F are NMR active. Within this work, $^1$H (proton) NMR is used to determine the microstructure of repeating units and composition of block copolymers. When exposed to an external magnet, nuclear spins within the sample align either with ($\alpha$ spin) or against ($\beta$ spin) the magnetic field. The sample is irradiated with a short radio pulse over the relevant range of frequencies. Lower energy nuclei are excited simultaneously and relax, releasing energy which is converted into a complex signal called a free induction decay (FID). The time domain FID can be converted into the frequency domain via a Fourier transform. Each proton is associated with a characteristic frequency depending on its chemical neighborhood and the applied magnetic field strength. For example, a proton next to a highly electronegative element comes into resonance at a higher frequency since the magnetic field of electrons opposes the external magnetic field. The actual magnetic field experienced by a proton with reduced surrounding electron density is higher; consequently, the greater energetic barrier between $\alpha$ and $\beta$ spins requires higher frequency radiation. By convention, the protons of tetramethylsilane are taken to be 0.0 ppm on the delta ($\delta$) scale. Chemical shifts of other protons are obtained by

$$\delta = \frac{v_{\text{sample}} - v_{\text{ref}}}{v_{\text{ref}}}$$

where $v_{\text{sample}}$ and $v_{\text{ref}}$ are the absolute resonance frequencies of the sample and NMR spectrometer, respectively. Here, the units of $\delta$ are ppm (parts per million) since the numerator is expressed in Hz while the denominator is expressed in MHz.
2.3 Proton nuclear magnetic resonance spectroscopy

Figure 2.3 Representative $^1$H NMR spectra from S, SI, and SISO aliquots. Additional peaks are observed in each subsequent spectrum as different monomers are incorporated into the block polymer. Protons corresponding to each relevant peak are labeled.
In this study, NMR spectra are obtained at room temperature from approximately 2 mM solutions of polymer in deuterated chloroform. Characteristic $^1$H NMR shifts pertaining to all block are shown in Figure 2.3. Since the molecular weight of the first block is obtained from SEC analysis, $^1$H NMR data on subsequent aliquots and the final tetrablock can be used to obtain tetrablock composition and molecular weight. This analysis relies on the fact that the area under each peak is proportional to the number of protons associated with the particular frequency. A sample calculation for SIS'O tetrablock is provided here. Since the $M_n$ of the initial PS block is known from SEC, NMR spectrum from the SI diblock is used to calculate number-average degree of polymerization for the poly(isoprene) block, $N_{n,\text{PI}}$:

$$N_{n,\text{PI}(1,4)} = \frac{5N_{PS}}{A_{PS}} A_{\text{PI}(1,4)}$$  \hspace{1cm} (2.7)

$$N_{n,\text{PI}(3,4)} = \frac{5N_{PS}}{A_{PS}} \frac{A_{\text{PI}(3,4)}}{2}$$  \hspace{1cm} (2.8)

where $N_{PS}$ is the number average degree of polymerization of the first poly(styrene) block and $A_{PX}$ is the area under the peak corresponding to the relevant repeat unit. $N_{PS'}$ can be computed from the SIS'O NMR spectrum:

$$N_{PS'} = \frac{A_{PS} N_{\text{PI}(1,4)}}{5A_{\text{PI}(1,4)}} - N_{PS}$$  \hspace{1cm} (2.9)

Finally, $N_{n,\text{PEO}}$ is calculated from the SIS'O NMR spectrum using:

$$N_{n,\text{PEO}} = \frac{A_{\text{PEO}} N_{\text{PI}(1,4)}}{4A_{\text{PI}(1,4)}}$$  \hspace{1cm} (2.10)

Once $N_n$ for all blocks have been computed using this technique, they can easily be converted to weight or volume fractions using monomer molecular weights and homopolymer densities from Fetters et al.\textsuperscript{167}
2.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal characterization technique used to locate the glass transition, melting temperature, and percent crystallinity in block polymers containing semicrystalline polymers. The glass transition or melting temperature establish the lowest temperature above which the phase behavior should be studied to avoid morphology disruption due to vitrification or crystallization of domains. A small quantity of the sample (5-10 mg) is sealed within a hermetic pan and subjected to a controlled heating rate. A second, equivalent pan is used as reference and the two pans are heated simultaneously. The heat flow to the sample is adjusted such that the temperature of both pans is equal. Relevant thermal transitions within the sample are characterized by a change in heat capacity. The DSC registers both the amount and direction (exothermic or endothermic) of the additional heat flow.

DSC measurements are typically carried out a heating rate of 10 °C/min. Faster heating rates yield a better signal to noise ratio since heat flow, the measured signal, increases with heating rate. In a typical experiment, the sample is heated above any relevant thermal transitions. A few minutes at elevated temperatures anneals the sample and erases the effects of prior stress and thermal history. The sample is then cooled to the starting temperature of the experiment. Data is collected during the second heating experiment. Glass transitions show up as step changes in the heat flow diagram while first order transitions, such as melting, show up as peaks (Figure 2.4). The glass transition temperature is identified at half the width of the step change while melting temperature is taken at the position of the melting peak. If the bulk heat of fusion ($\Delta H_{m, bulk}$) is known, the percent crystallinity ($X_c$) can be determined by

$$X_c = \frac{\Delta H_{m, exp}}{\Delta H_{m, bulk} W_c}$$  \hspace{1cm} (2.11)
where $\Delta H_{m,exp}$ is the experimentally measured heat of fusion of the sample and $w_c$ is the weight fraction of the semicrystalline block. The sample heat of fusion can be obtained by integrating the total area under the melting peak.

**2.5 Dynamic mechanical spectroscopy**

Dynamic mechanical spectroscopy (DMS) or rheology is a technique used to probe the viscoelastic properties of polymeric materials.\textsuperscript{168} In purely elastic materials, shear stress $\sigma$ is related to strain $\gamma$ through

$$
\sigma = \hat{G}\gamma
$$

where $\hat{G}$ is the elastic modulus and acts as a spring constant. In contrast, shear stress in a purely viscous liquid is related to the time derivative of strain (strain rate, $\dot{\gamma}$) through

$$
\sigma = \eta\dot{\gamma}
$$

where $\eta$ is the viscosity and represents the amount of energy dissipated through molecular motion. Polymers combine the responses of both viscous liquid and elastic
solids. When subjected to an instantaneous deformation, polymer chains extend away from the equilibrium confirmation, resulting in a loss of entropy. However, after a characteristic time, the stored elastic energy can be dissipated as the chains relax back to their equilibrium positions. This behavior gives polymer their unique viscoelastic nature which leads to a stress response intermediate to the elastic and viscous limits.

The simplest model which can capture this behavior is the Maxwell model. The Maxwell element is a Hookean spring (with spring constant $G$) connected in series with a Newtonian dashpot (of viscosity $\eta$). If a sinusoidal strain of the form $\gamma_0 \sin(\omega t)$, where $\omega$ is the frequency and $t$ is time, is applied to the element, the resulting stress is

$$\sigma(t) = G' \sin(\omega t) + G'' \cos(\omega t)$$

where $G' = \frac{G \omega^2 \tau^2}{1 + \omega^2 \tau^2}$, $G'' = \frac{G \omega \tau}{1 + \omega^2 \tau^2}$, and $\tau = \frac{\eta}{G'}$. Examining the equation, it becomes clear that it has two contributions: one in-phase with strain and one out-of-phase with the imposed strain. The in-phase component is characterized by $G'$ (elastic or storage modulus) and the out-of-phase component is characterized by $G''$ (viscous or loss modulus).

Though the Maxwell model is a poor representation of real polymers, it still captures many important fundamental concepts. Firstly, it yields a characteristic time for the system, $\tau$. In reality, the large size of polymer chains leads to a broad spectrum of relaxation times which can be captured by more sophisticated formulations such as the Rouse model. In homopolymers, these characteristic relaxation times correspond to processes which occur at different length scales. High frequencies (or small time scales) probe small length scales. At such frequencies, the Maxwell model predicts a solid-like response where the stress is independent of frequency. Low frequencies (or large time scales) allow the polymer chains to relax leading to a distinctly liquid-like response. At low (or terminal) frequencies, the following scaling laws are correctly predicted by the Maxwell model: $G' \sim \omega^2$ and $G'' \sim \omega^1$. 
2.5 Dynamic mechanical spectroscopy

The viscoelastic response of block copolymers is highly dependent on the state of order. In the disordered state, block copolymers display the properties of a viscoelastic liquid and terminal scaling \((G' \sim \omega^2\text{ and } G'' \sim \omega^1)\). However, while in the ordered phase, rheological behavior mimics that of a viscoelastic solid with exact scaling dependent on the details of mesoscopic order. Cubic phases exhibit a solid-like response \((G' \sim \omega^0)\) due to the three-dimensional nature of these morphologies.\(^{169}\) However, lamellar and cylindrical morphologies exhibit intermediate responses. Experiments on lamellar samples\(^{42,170-173}\) have yielded the scaling \(G' \sim G'' \sim \omega^{1/2}\) while polydomain hexagonal cylinders exhibit the scaling \(G' \sim G'' \sim \omega^{1/3}\).\(^{174,175}\)

Since rheological tests can be used to gauge the state of order, a variety of tests are used in this work to identify temperatures associated with an order-disorder transition \((T_{ODT})\) or order-order transitions \((T_{OOT})\). Isochronal temperature ramps measure \(G'\) and \(G''\) while heating or cooling the sample at a constant rate. A precipitous drop in \(G'\) is indicative of the transition from an ordered state to the disordered phase.\(^{176,177}\) Transitions from an ordered phase to another can also be observed, though they may sometimes be obscured by slow kinetics or negligible changes in modulus.\(^{178,179}\) Alternatively, viscoelastic properties can be probed through isothermal frequency sweeps which record \(G'\) and \(G''\) as a function of frequency over a broad range of temperatures. These data can be superimposed along the frequency axis using shift factors \(\alpha_T(T)\) to create a master curve at a reference temperature \(T_{ref}\). This process, called time-temperature superposition (TTS), necessitates that all relaxation times have the same temperature dependence, an assumption not strictly valid for block polymers.\(^{180}\) However, in this work, TTS is used only to facilitate comparison of data obtained over a broad range of temperatures. Representative data from both rheological experiments are illustrated in Figure 2.5. DMS data can be quite useful in informing further experiments but complementary data from SAXS and TEM is needed to conclusively comment on morphological behavior.
2.6 Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) is perhaps the most important tool in determining the morphology of a block polymer melt. The underlying physical principles are the same as in light scattering or small-angle neutron scattering, but the causes of scattering differ. While light scatters due to refraction index fluctuations, X-rays interact with electron clouds and, therefore, scatter due to electron density differences. In this
2.6 Small-angle X-ray scattering

work, synchrotron SAXS is used to elucidate the symmetry of tetrablock terpolymer morphologies and extract information about lattice parameters. When the propagating plane wave interacts with the polymer sample it is scattered, resulting in a spherical wave radiating from each scattering site. The scattering can arise from random fluctuations within the material (incoherent) or spatial correlations between monomers and polymer (coherent). Incoherent scattering is generally not considered because the wavelength shift is negligible at small angles. The coherent elastic scattering intensity is a product of the form and structure factors. The form factor is an interference pattern whose oscillations are typical of the domain structure (e.g., cylinder vs. sphere) while the structure factor contains information related to the spatial arrangement of these domains (e.g., BCC vs. FCC). The coherent scattering pattern is a Fourier transform of the pair correlation function of scatterers. Thus, reciprocal space data from SAXS, when combined with real space micrographs from TEM, can yield valuable insight into the crystalline structure of a block polymer melt.

The interplanar spacing \(d\) in an ordered block copolymer melt can be quite large when compared to atomic or molecular analogs. At this scale, the diffraction of X-ray radiation at very small angles \(\theta\) is ideal for probing structure as per Bragg’s law\(^1\):

\[
n\lambda = 2\pi \sin\left(\frac{\theta}{2}\right)
\]

(2.15)

where \(\lambda\) is the wavelength of the incident radiation. These relevant experimental quantities can be conveniently described by the scattering wave vector:

\[
|\vec{q}| = q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)
\]

(2.16)

Here, \(q\) has units of inverse length. The direction of the scattering wave vector corresponds to the normal to the plane of scatterers. A vector pointing in this direction with the magnitude \(2\pi/d\) is called the reciprocal lattice vector. The Bragg condition for diffraction is automatically satisfied when the magnitude of these two vectors coincides. Thus, Bragg diffraction takes place when scattering wave vector (determined by experimental setup) matches the reciprocal lattice vector (determined by sample) as shown below.
2.6 Small-angle X-ray scattering

\[ q_{hkl} = \frac{2\pi}{d_{hkl}} \]  \hspace{1cm} (2.17)

where \( d_{hkl} \) is the interplanar spacing of the plane with Miller indices \( h, k, \) and \( l \).

Expressions relating Miller indices and lattice parameters to the relevant domain spacing are available for a variety of existing block copolymer morphologies. For example, in the 1D lamellar case, there is only one Miller index and the interplanar spacing is given by

\[ \frac{1}{d_{LAM}} = \sqrt{\frac{h^2}{a^2}} \]  \hspace{1cm} (2.18)

where \( a \) is the primary domain spacing. All values of \( h \) are allowed resulting in peaks at \( (q/q^*) = 1, 2, 3, 4 \ldots \) where \( q^* = q_1 = \left(\frac{2\pi}{a}\right) \) is defined as the principal peak. However, in the case of precise volumetric symmetry, structure factor extinction eliminates the even peaks.\(^{136} \) In the 2D case of hexagonally packed cylinders, two Miller indices are required and the interplanar spacing is given by

\[ \frac{1}{d_{HEX,2D}} = \sqrt{\frac{h^2 + k^2 + hk}{a^2}} \]  \hspace{1cm} (2.19)

where \( a \) is the lattice parameter of the 2D hexagonal unit cell and equal to the domain spacing at \( q^* = q_{10} \). The symmetry of the lattice allows all possible combination of \( h \) and \( k \) resulting in peaks at \( q/q^* = 1, 3, 4, 7, 9 \ldots \) This can be extended to the 3D hexagonal lattice as well and the domain spacing is given by

\[ \frac{1}{d_{HEX,3D}} = \sqrt{\frac{4(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}} \]  \hspace{1cm} (2.20)

where \( a \) is the lattice parameter orthogonal to the six-fold axis and equal to the domain spacing at \( q^* = q_{100} \). Here we encounter the fact that Bragg diffraction is a necessary but insufficient condition for observing reflections in the SAXS pattern. The symmetry of the particular crystal may lead to additional systematic absences. For example, in the
Table 2.1 Summary of allowed reflections for phases commonly seen in this thesis.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Extinction Conditions</th>
<th>Allowed Reflections</th>
<th>Relative Peak Positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAM</td>
<td>All allowed</td>
<td>(1), (2), (3), (4),…</td>
<td>1, 2, 3, 4</td>
</tr>
<tr>
<td>HEXC</td>
<td>All allowed</td>
<td>(10), (11), (20),</td>
<td>1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$,…</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(21), (30),…</td>
<td></td>
</tr>
<tr>
<td>BCC</td>
<td>$h + k + l = \text{odd}$</td>
<td>(110), (200), (211), (220), (310),…</td>
<td>1, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$,$\sqrt{6}$,$\sqrt{7}$,…</td>
</tr>
<tr>
<td>FCC</td>
<td>$h,k,l$ mixed</td>
<td>(111), (200), (220), (222), (311),…</td>
<td>$\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$, $\sqrt{6}$,$\sqrt{8}$,$\sqrt{10}$,$\sqrt{11}$,$\sqrt{12}$,$\sqrt{16}$,…</td>
</tr>
<tr>
<td>HCP</td>
<td>$h + 2k = 3n$ with $l$ odd</td>
<td>(100), (002), (101), (102), (110),…</td>
<td>N/A</td>
</tr>
<tr>
<td>A15</td>
<td>If $00l$ or $hh+l = 2n$ all other allowed</td>
<td>(110), (200), (210), (211), (220),…</td>
<td>$\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$,$\sqrt{6}$,$\sqrt{8}$,$\sqrt{10}$,$\sqrt{11}$,$\sqrt{12}$,$\sqrt{16}$,…</td>
</tr>
<tr>
<td>σ phase</td>
<td>If $h0l$ or $0hl$: $h + l = 2n$ If $h00$ or $00l$: $h,l = 2n$ all other allowed</td>
<td>(110), (200), (101), (210), (111),…</td>
<td>N/A</td>
</tr>
</tbody>
</table>

For hexagonally close packed lattice, reflections for planes where $h + 2k = 3n$ and $l$ is odd are forbidden by the symmetry of the lattice ($n$ is any whole number). Reflection conditions for all lattices are summarized in Table 2.1. Since the 3D hexagonal unit cell has two lattice parameters, peaks do not appear at fixed values of $q/q^*$. In contrast, cubic phases (BCC, FCC, A15) have only one lattice parameter $a$, and the domain spacing is given by:

$$\frac{1}{d_{CUB}} = \sqrt{\frac{h^2 + k^2 + l^2}{a^2}} \quad (2.21)$$

Thus, relative peak ratios for cubic phases can be obtained and are also summarized in Table 2.1 Finally, the σ phase has a 3D tetragonal unit cell whose domain spacing for each $hkl$ is given by:
2.7 Transmission electron microscopy

\[
\frac{1}{d_{TET}} = \sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}
\]

(2.22)

where \(a\) and \(c\) are the lattice parameters. Possible reflection conditions for all space groups are reported in the International Tables for Crystallography.\(^{181}\)

As seen from the preceding discussion, diffraction is an arranged event in which the scattering wave vector and reciprocal lattice vector must be matched. If the condition is not met exactly, the crystal must be rotated to the correct \(\theta\) value for diffraction to occur. In the experiments reported here, the block copolymer does not exist as a single crystal, but a mixture of numerous grains in which all orientations are equally likely. Thus, the scattering experiment samples a wide variety of crystallite orientations and generates a powder pattern composed of concentric Debye-Scherrer rings with uniform intensity at radii \(q_{hkl}\), as shown in Figure 2.6. These two dimensional patterns are averaged over all azimuthal angles to obtain the 1D pattern of intensity vs. \(q\). If the 2D pattern displays rings of inconsistent intensity, then the integration will not be representative of the intensities seen in the averaged powder pattern. In this thesis, SAXS data is supplemented with real space transmission electron microscopy images whenever possible to unambiguously identify domain geometry and ordering symmetry.

2.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is used to probe real-space structures on a sub-micron size level. The principles are analogous to conventional light microscopy; however, the illumination is provided by electrons, the lenses are electromagnetic coils, and visualization is achieved through use of an electron-luminescent screen or a charge-coupled device (CCD) detector. The microscope can be split into four major sections: an illumination system, a specimen stage, an imaging system, and the image recording system.

In the illumination system, an electron beam is generated from an energized filament and accelerated by applying a voltage (HT), typically between 20 and 300 kV. This section of the microscope is fitted with condenser lenses and apertures. The first
Figure 2.6 (a) Illustration of Bragg’s law with incident wave vector $k_i$, scattered wave vector $k_s$, and interplanar spacing $d$ demonstrates the geometrical condition necessary to observe diffraction peaks. The planes shown in (a) may, as an example, be visualized as (b) the (002) planes of the BCC lattice. (c) Simplified SAXS experiment setup. The 2D pattern obtained here is (d) azimuthally averaged to obtain a 1D pattern. Diffraction peaks yield information about interplanar spacing and aid in identification of the lattice symmetry.
condenser lens (C1) adjusts the original beam diameter while the second condenser lens (C2) adjusts the illumination spread. An aperture located at C2 eliminates high angle electrons, increasing spatial coherence and enhancing contrast. A larger C2 aperture causes a larger area of contact between the electron beam and specimen resulting in background scatter that decreases image contrast.

After the beam is optimized, it reaches the specimen and is absorbed, scattered, or transmitted. There are several methods of generating contrast within the specimen and the primary method utilized here is mass contrast. The strength of interaction between the electron beam and sample atoms is directly proportional to \( Z \), the atomic number. Since polymer blocks are comprised mostly of carbon \((Z = 6)\) and hydrogen \((Z = 1)\), a staining agent is required. In this work, the staining agent osmium tetroxide (OsO\(_4\)) reacts chemically with the double bonds in the poly(isoprene) domains imparting mass contrast between PI and the unstained PS and PEO domains.\(^{131}\) The production of uniformly thin sections (~60 nm) using a microtome is extremely important to ensure sufficient transmitted beam intensity.

The first component of the imaging system is the objective lens which focuses the scattered electrons onto an image plane. Image quality is improved by the following aperture which eliminates scattered electrons and reduces background intensity. However, transmitted beam intensity is also reduced, lowering overall image brightness. Though smaller apertures are preferred, the user must find the optimal balance which produces an image with sufficient contrast. A computer-based user interface is used to collect the final digital images obtained through a CCD detector. In this work, the obtained images undergo minor edits to enhance brightness and optimize contrast. These real space images are a valuable asset in illuminating the mesoscopic structure of block polymer melts. However, the limitations of trying to understand three dimensional phases using images that are two dimensional projections should be considered. Overreliance on TEM has led to erroneous space group assignment in the past\(^{63,64,182–184}\), reinforcing the need to complement these micrographs with SAXS and DMS experiments.
Chapter 3

Synthesis Techniques for the Generation of ABCA′-type Tetrablock Terpolymers*,†

3.1 Introduction

Self-assembly of block copolymer melts into microphase separated, ordered structures can generate materials that exhibit rich phase behavior.29 The simplest of linear block copolymers, an AB diblock, has at least four stable phases (lamellae, gyroid, cylinder, and spheres).33 A combination of extensive experimental and theoretical efforts has led to a deeper understanding of diblock phase behavior, though new forms of self-assembly continue to be found.92,93 However, the number of ordered structures in a block copolymer system increases rapidly as the number of blocks (n) and types of blocks (k) are increased.11 Therefore, tetrablock terpolymers (n=4, k=3) present a massive parameter space with exciting opportunities for formation of novel self-assembling soft materials. Experiments on ABAC tetrablock terpolymers have already revealed rich phase behavior. Exotic morphologies, including the Frank-Kasper sigma phase and a dodecagonal quasicrystalline morphology have been reported in sphere-forming poly(styrene)-

* This work was done in collaboration with Dr. Athanasios Touris.
†A. Touris†, S. Chanpuriya†, M. A. Hillmyer and F. S. Bates, Polym. Chem., 2014, 5, 5551 - Reproduced by permission of The Royal Society of Chemistry († Contributed equally)
3.1 Introduction

*b-poly(isoprene)-* *b-poly(styrene)-* *b-poly(ethylene oxide)* (SISO) tetrablocks.\textsuperscript{141–143}

Clearly, intelligent manipulation of the large parameter space associated with tetrablock terpolymers will lead to materials with specific domain geometry and packing symmetry. The interesting phase behavior observed in ABAC systems has prompted speculation on the ordered structures that may be formed by ABCA tetrablock terpolymers. Although a few studies have been reported on the self-assembly of ABCA tetrablocks in solution, this class of polymers still remains largely unexplored.\textsuperscript{163,185} Of particular interest are asymmetric ABCA’ tetrablocks (where the prime symbol signifies unequal A block lengths). ABCA’ polymers, with highly incompatible middle blocks may lead to unique geometries such as axially and radially segregated cylinders and Janus spheres.\textsuperscript{11} In addition, the ordering symmetry of these structures may be controlled by varying the symmetry parameter, $\xi = N_A/N_A'$, where $N_A$ is the length of the A block. If the individual blocks (and, consequently, their degree of incompatibility) and $\xi$ are systematically tuned, ABCA’ tetrablocks may enable independent control over domain geometry and ordering symmetry leading to exciting new morphologies that can have various practical applications.\textsuperscript{11}

Of particular interest and significance are the non-centrosymmetric structures that may be formed by these asymmetric ABCA’ tetrablocks. Since block copolymers self-assemble into microphase separated structures with nanoscopic periodicity on the order of 10-100 nm, they make excellent candidates for synthesizing soft materials that lack a center of symmetry and possess well-defined long-range periodicity. This non-centrosymmetry allows dipolar molecules to display useful properties such as nonlinear optical activity and piezo- and pyroelectricity.\textsuperscript{186,187} Successful synthesis of layered non-centrosymmetric structures has already been reported in blends of ABC triblocks and AB diblocks as well as ABCD and symmetric ABAC tetrablocks.\textsuperscript{140,187,188} Asymmetric ABCA’ tetrablocks may allow for the generation of non-centrosymmetric structures beyond these layered, lamellar materials. As the incompatibility between the middle two blocks (B and C) is increased, the microstructure may transition from lamellar to cylinders and finally to spheres in order to minimize unfavorable contacts between
incompatible blocks, allowing control over domain geometry.\textsuperscript{11,140,189} Inducing molecular asymmetry ($\xi \neq 1$) may provide control over the ordering symmetry of these domains as longer corona chains will favor packing near shorter corona chains. This tendency to minimize unfavorable chain stretching and compression at constant density may lead to the formation of exciting new morphologies such as cubic order of Janus particles.\textsuperscript{11} The hypothesized phase behavior of these materials is illustrated in Figure 3.1.

Only a few synthetic methods have been reported in the literature to produce ABCA type tetrablocks. Poly(styrene)-\textit{b}-poly(isoprene)-\textit{b}-poly(butadiene)-\textit{b}-poly(styrene) (SIBS) tetrablocks were synthesized using sequential anionic polymerization.\textsuperscript{185} Though this method can produce tetrablocks of any asymmetry, the choice of monomers is severely limited due to the inherent constraint in anionic polymerization that requires stability of the second block carbanion to equal or exceed that of the preceding block.\textsuperscript{1} This limitation can be overcome by using synthetic strategies that couple AB with CA’ diblocks (or ABC triblocks with A’ homopolymers). Such a route enabled the production of poly(isoprene)-\textit{b}-poly(styrene)-\textit{b}-poly(2-vinylpyridine)-\textit{b}-poly(isoprene) (ISPI). IS diblocks end-functionalized with a diphenylethylene group were reacted with living IP diblocks with the active site on the chain end of poly(2-vinylpyridine) to yield the ISPI tetrablock.\textsuperscript{140} Additionally, poly(ethylene oxide)-\textit{b}-poly(styrene)-\textit{b}-poly(butadiene)-\textit{b}-poly(ethylene oxide) (OSBO) were produced by sequential addition of styrene and butadiene to the protected initiator 3-tert-butyldimethylsiloxysilox-1-propyllithium, followed by termination with ethylene oxide and HCl. After deprotection using tetra(n-butyl)ammonium fluoride (TBAF), reinitiating the diblock in THF with potassium naphthelanide (KNaph) and reacting with ethylene oxide yielded symmetric OSBO tetrablocks.\textsuperscript{163} A similar route that enabled the production of asymmetric OSBO’ tetrablocks involved using triisopropylsiloxy-1-propyllithium as a protected initiator for the anionic polymerization of styrene and butadiene, and diphenylmethyl potassium as the base activator for the polymerization of ethylene oxide. Deprotection of the $\alpha$–(TIPS-hydroxyl) using TBAF followed by reinitiation using KNaph and subsequent polymerization of ethylene oxide yielded asymmetric OSBO’ tetrablocks.\textsuperscript{189} This strategy
3.1 Introduction

Figure 3.1 (a) Hypothetical self-assembly of ABCA' tetrablock terpolymers at constant composition. As $\chi_{BC}/\chi_{AB}$ increases, the system should decrease interfacial surface area ratio ($A_{BC}/A_{AC}+A_{AB}$) to minimize interfacial energy. This will drive morphological transitions from lamellae to radially and axially segregated cylinders to Janus spheres. (b) This simplified diagram illustrates how, when $\xi = 1$, the cylinders may not show axial order as the equal length corona chains do not influence cylinder packing. (c) When $\xi > 1$, longer chains packing near each other is not favored. Thus, the system may pack longer chains emanating from the C block closer to shorter chains emanating from the B block inducing axial order. Note that axial ordering cannot accommodate the 6-fold rotational symmetry usually associated with hexagonal packing of cylinders driving a transition to 4-fold rotationally symmetric packing of cylinders. From Bates et al. Science 2012, 336, 434–440. Adapted with permission from AAAS.
forms the starting point for the generation of asymmetric LSBL’ tetrablocks reported below.

Here, two versatile synthetic routes are presented that further expand the range monomers which can be used to produce asymmetric tetrablock terpolymers. Specifically, a novel synthetic route for the generation of a poly(lactide)-b-poly(styrene)-b-poly(butadiene)-b-poly(lactide) (LSBL’) tetrablock terpolymer with asymmetrically sized polylactide end blocks is described using a hydroxyl functionalized anionic initiator and a Sc(OTf)$_3$ catalyzed selective deprotection reaction. Poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide)-b-poly(styrene’) (SIO’S’) tetrablocks were synthesized using a combination of anionic polymerization and RAFT. Hydroxyl terminated SIO triblocks are synthesized through anionic polymerization and subsequently converted to macro chain transfer agents used to polymerize the final styrene block using RAFT.

3.2 Methods

3.2.1 Materials

Standard Schlenk techniques and equipment were used to manipulate all moisture- and air-sensitive compounds under a high-purity argon atmosphere.$^{190}$ Styrene (Aldrich, $\geq 99\%$), butadiene (Aldrich, $\geq 99\%$), isoprene (Acros, $\geq 99\%$) and ethylene oxide (Aldrich, $\geq 99.5\%$) were purchased from Aldrich and purified according to protocols described elsewhere.$^{191}$ The preparation of 3-triisopropylsilyloxy-1-propyllithium (TIPSOPrLi) was reported elsewhere.$^{192}$ Potassium naphthalenide (NaphK) resulted from the reaction of potassium with a 10% molar excess of naphthalene in tetrahydrofuran (THF) at room temperature for 24 hours. Cyclohexane was purified by sparging with argon followed by sequential passage through activated alumina and supported copper catalyst to remove protic impurities and trace oxygen.$^{193}$ Tetrahydrofuran was purified by sparging with argon and subsequent passage through two columns containing activated alumina. Dichloromethane was stirred over CaH$_2$ for several days and then distilled. $N,N,N',NN'$-Tetramethylethylene diamine (TMEDA, Aldrich, $\sim 99\%$) was exposed to a sodium mirror prior to distillation. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, $\sim 98\%$) was stirred over CaH$_2$ and distilled prior to use. Azobisisobutyronitrile (AIBN) was
recrystallized twice from methanol. (±)-Lactide (Purac) was recrystallized twice from toluene prior to being stored in a glovebox. Lithium with high sodium content (0.5 - 1 %) and all other chemicals were purchased from Aldrich and used as received.

3.2.2 Molecular Characterization

Standard $^1$H NMR spectra in CDCl$_3$ were acquired on a Varian VI-500 spectrometer and were referenced to the residual solvent peak. Size-exclusion chromatography (SEC) analysis was performed on three Phenogel (Phenomenex) columns (1000, 5000 and 500 Å pore size) with THF eluent at 25 °C with a flow rate of 1.0 mL/min controlled by a Waters 590 Programmable HPLC pump using a Waters 717 Autosampler and a Waters 410 Refractometer. The reported SEC data for all polymers have been normalized using the maximum peak intensity of each trace.

3.2.3 Poly(lactide)-b-poly(styrene)-b-poly(butadiene)-b-poly(lactide′) Synthesis

**TIPS-O-SB-OH Synthesis.** Anionic polymerization of styrene (151 mmol) was initiated by TIPSOPrLi (2.39 mmol) in cyclohexane (300 mL) containing TMEDA (7.20 mmol) and thermostated at 40 °C. After 1 h, butadiene (268 mmol) was added and was allowed to react for 1.5 h at 40 °C, followed by the addition of 68.2 mmol of ethylene oxide. The reaction was allowed to stir overnight and then was terminated by the addition of degassed methanol. The polymer was isolated by precipitation in cold methanol and dried overnight under vacuum followed by dissolution in dichloromethane and passage through a silica column to remove any polar impurities. The solvent was removed using a rotary evaporator and then the polymer was freeze-dried from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.00 ppm (br, -Si(CH)$_3$CH$_3$)$_6$, 1.10-2.21 ppm (m, aliphatic main chain), 3.50 ppm (br, -CH$_2$OSi(CH)$_3$CH$_3$)$_6$, 3.66 ppm (br, -CH$_2$OH), 4.86-5.05, 5.27-5.66 ppm (m, unsaturated non aromatic), 6.33-7.25 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.2 and 3.3, respectively.

**TIPS-O-SBL′′-OH Synthesis.** In an argon filled glovebox, a 100 mL round bottom flask was charged with 4.5 g of TIPS-O-SB-OH (0.375 mmol), 60 mL of dichloromethane, 3.2 g of (±)-lactide (22.2 mmol) and finally 0.11 mL (0.736 mmol) of
3.2 Methods

Figure 3.2 Representative SEC chromatographs of intermediate products and final LSBL’ tetrablock terpolymer.

DBU. The flask was capped with a septum and the solution was stirred at room temperature for 20 min prior to addition of 0.23 g (1.88 mmol) of benzoic acid to quench the reaction. The polymer was isolated by precipitation in cold methanol and was freeze-dried from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.00 ppm (br, -Si(CH$_3$)$_3$CH$_3$)$_6$), 1.12-2.23 ppm (m, aliphatic main chain), 3.50 ppm (br, -CH$_2$OSi(CH$_3$)$_3$CH$_3$)$_6$), 4.33 ppm (br, -CH(CH$_3$)OH), 4.85-5.06, 5.27-5.66 ppm (m, unsaturated non aromatic), 5.12-5.24 ppm (methine polylactide protons), 6.32-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.2 and 3.3, respectively.

**HO-SBL’’-OH synthesis.** In a 100 mL two necked flask 3.0 g of TIPS-O-SB-OH (0.146 mmol) were dissolved under argon in a mixture of acetonitrile (30 mL) and THF (30 mL). 0.036 g (0.073 mmol) of Sc(OTf)$_3$ were added, the flask was sealed and the solution was stirred at room temperature for 2 days. The polymer was isolated by precipitation in cold methanol and was freeze-dried from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 0.98-2.24 ppm (m, aliphatic main chain), 3.45 ppm (br, -CH$_2$OH), 4.33 ppm (br, -CH(CH$_3$)OH), 4.84-5.07, 5.27-5.65 ppm (m, unsaturated non aromatic), 5.13-5.25 ppm (methine polylactide protons), 6.29-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.2 and 3.3, respectively.
Figure 3.3 Representative $^1$H NMR spectra of all intermediate products and final LSBL’ tetra-block terpolymer.
3.2 Methods

**LSBL′ synthesis.** HO-SBL′′-OH, the deprotected analog of TIPS-O-SBL′′-OH, was used as the macroinitiator for LSBL′ synthesis. A similar procedure as in the case of TIPS-O-SBL′′-OH was followed. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 0.98-2.25 ppm (m, aliphatic main chain), 4.36 ppm (br, -CH(CH$_3$)OH), 4.83-5.05, 5.28-5.64 ppm (m, unsaturated non aromatic), 5.12-5.27 ppm (methine polylactide protons), 6.28-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.2 and 3.3, respectively.

**First Control Experiment: TIPS-O-S-synthesis.** Anionic polymerization of styrene (29.8 mmol) was initiated by TIPSOPrLi (0.392 mmol) in cyclohexane (50 mL) containing TMEDA (1.96 mmol) and thermostated at 40 °C. After 1 h the reaction was terminated by the addition of degassed methanol. The polymer was isolated by precipitation in cold methanol and was freeze-dried from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.00 ppm (br, -Si(CH)$_3$CH$_3$)$_6$), 1.20-2.13 ppm (m, aliphatic main chain), 3.50 ppm (br, -CH$_2$OSi(CH)$_3$CH$_3$)$_6$), 6.28-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.4 and 3.5, respectively.

**First Control Experiment: HO-S synthesis.** A similar procedure as in the case of HO-SBL′′ was followed. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.20-2.13 ppm (m, aliphatic main chain), 3.45 ppm (br, -CH$_2$OH), 6.27-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.4 and 3.5, respectively.

**First Control Experiment: LS Synthesis.** A similar procedure as in the case of LSBL′ was followed. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.20-2.13 ppm (m, aliphatic main chain), 3.91 ppm (br, -CH$_2$O-), 4.34 ppm (br, -CH(CH$_3$)OH), 5.12-5.31 ppm (methine polylactide protons), 6.25-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.4 and 3.5, respectively.

**Second Control Experiment: TIPS-O-SBL′′-OH synthesis.** TIPS-O-SBL′′-OH was used as the macroinitiator for the polymerization of (±)-lactide. The same procedure was followed as in the case of TIPS-O-SBL′′-OH. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.00 ppm (br, -Si(CH)$_3$CH$_3$)$_6$), 1.12-2.24 ppm (m, aliphatic main chain), 3.50 ppm (br, -CH$_2$OSi(CH)$_3$CH$_3$)$_6$), 4.34 ppm (br, -CH(CH$_3$)OH), 4.85-5.06, 5.25-5.67 ppm (m,
3.2 Methods

Figure 3.4 SEC analysis for the control experiments to check the α,ω-hydroxyl chain end functionalities.

Figure 3.5 $^1$H NMR end group analysis for the control experiment of the α-hydroxyl end group.
unsaturated non aromatic), 5.10-5.24 ppm (methine polylactide protons), 6.30-7.26 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.4 and 3.5, respectively.

3.2.4 Poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide)-b-poly(styrene′) Synthesis

**SI-OH Synthesis.** Anionic polymerization of styrene (111 mmol) was initiated by s-BuLi (1.32 mmol) in cyclohexane (200 mL) thermostated at 40 °C. The reaction was allowed to stir overnight and then isoprene (142 mmol) was added and was allowed to react for the same amount of time at 40 °C, followed by the addition of 2 mL of ethylene oxide (EO). The reaction was allowed to stir overnight and then was terminated by the addition of degassed acidic methanol. The polymer was isolated by precipitation in cold methanol, followed by freeze-drying from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.75-2.25 ppm (m, aliphatic main chain), 3.63 ppm (br, -CH$_2$OH), 4.64-4.86, 5.02-5.27 ppm (m, unsaturated non aromatic), 6.28-7.27 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.6 and 3.7, respectively.

**SIO-OH Synthesis.** In a typical reinitiation reaction$^{194}$, 10 g (0.610 mmol) of SI-OH were dissolved in 200 mL of THF and the solution was thermostated at 40 °C. Then, the polymer solution was slowly titrated with freshly prepared potassium naphthalenide solution until a light green color persisted for at least 30 min. The EO (132 mmol) was added turning the reaction mixture colorless and was allowed to stir for 20 h, before it was terminated by the addition of degassed acidic methanol. The crude product was isolated by precipitation in cold isopropanol and was freeze-dried from benzene. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 1.22-2.25 ppm (m, aliphatic main chain), 3.63 ppm (br, PEO backbone protons), 4.64-4.82, 5.02-5.27 ppm (m, unsaturated non aromatic), 6.28-7.27 ppm (m, aromatic). SEC and $^1$H NMR data are shown in Figures 3.6 and 3.7, respectively.
3.2 Methods

Figure 3.6 Representative SEC chromatographs of intermediate products and final SIOS’ tetrablock terpolymer.

S-1-dodecyl-S’-(α,α’-dimethyl-α”-acetic acid) trithiocarbonate (CTA) synthesis.

The starting point for the synthesis of the CTA agent was achieved following a published procedure. A vital difference from the referenced literature was that no phase transfer catalyst was used which, on the one hand, simplified the reaction to a one step process and, on the other hand, facilitated isolation of the final product. 1-Dodecanethiol (20.0 g, 0.098 mol), acetone (158.2 g, 2.72 mol), carbon disulfide (8.30 g, 0.109 mol) and chloroform (28.8 g, 0.241 mol) were mixed in a jacketed reactor cooled to 10 °C under inert gas. Potassium hydroxide solution (50%, 0.891 mol) was added drop wise over 4 h, during which time the color turned red. The reaction was stirred overnight at room temperature. 36 mL of water was added, followed by addition of concentrated HCl until the pH=2. After stirring the solution overnight, the acetone was evaporated and the precipitated solid was collected with a Buchner funnel and then stirred in 250 mL of 2-propanol. The undissolved solid was filtered off the 2-propanol solution was concentrated to dryness, and the resulting solid was recrystallized from hexanes to afford a yellow crystalline solid. $^1$H NMR (500 MHz, CDCl$_3$, 21 °C): 0.88 (t, 3H), 1.20-1.42 (m, 20H), 1.73 (s, 6H), 3.28 (t, 2H).
Figure 3.7 Representative $^1$H NMR spectra of all intermediate products and final SIOS’ tetrablock terpolymer.
3.3 Results and Discussion

**SIO-CTA synthesis.** CTA (2.17 g, 5.9 mmol) was mixed with excess oxalyl chloride (5.1 mL, 61 mmol) in dry CH₂Cl₂ (30 mL) under an inert atmosphere and stirred at room temperature for 4 h. CH₂Cl₂ and excess oxalyl chloride were removed under vacuum. SIO (15 g in 120 mL of CH₂Cl₂, 0.60 mmol) was added, and the reaction mixture was stirred at room temperature overnight. The polymer was precipitated in cold isopropanol twice and then was freeze dried from benzene. **¹H NMR (500 MHz, CDCl₃, 21 °C):** 1.20-2.27 ppm (m, aliphatic main chain), 3.26 ppm (t, -S-CH₂-C₁₁H₂₃), 3.63 ppm (br, PEO backbone protons), 4.26 ppm (t, -CH₂-O-), 4.63-4.79, 5.04-5.22 ppm (m, unsaturated non aromatic), 6.28-7.27 ppm (m, aromatic). SEC and **¹H NMR data are shown in Figures 3.6 and 3.7, respectively.**

**SIOS’ synthesis.** SIO-CTA macroinitiator (0.1 g, 4x10⁻³ mmol), styrene (0.45 g, 4.3 mol), and AIBN (6.5x10⁻² mg, 0.4*10⁻³ mmol) were dissolved in toluene (0.45 mL). The solution was bubbled with argon for 15 min, and then reacted at 80 °C for 8 h. The reaction was quenched by cooling the reactor down to 0 °C. The reaction mixture was precipitated in cold isopropanol and dried overnight under vacuum. **¹H NMR (500 MHz, CDCl₃, 21 °C):** 1.18-2.30 ppm (m, aliphatic main chain), 3.28 ppm (br, -S-CH₂-C₁₁H₂₃), 3.63 ppm (br, PEO backbone protons), 4.28 ppm (br, -CH₂-O-), 4.64-4.77, 5.06-5.23 ppm (m, unsaturated non aromatic), 6.25-7.27 ppm (m, aromatic). SEC and **¹H NMR data are shown in Figures 3.6 and 3.7, respectively.**

3.3 Results and Discussion

3.3.1 Synthesis of LSBL’ asymmetric tetrablock terpolymers

The general reaction scheme used to generate the asymmetric tetrablock terpolymer is presented in Figure 3.8. A poly(styrene)-b-poly(butadiene) diblock copolymer was prepared in cyclohexane using a hydroxyl-functionalized 3- triisopropylsilyloxy-1-propyllithium (TIPSOPrLi) initiator by sequentially adding styrene and butadiene in the presence of TMEDA, which accelerates the initiation and propagation rates. The poly(styrene)-b-poly(butadiene) chains were capped with ethylene oxide (EO) yielding a α-(TIPS-hydroxyl)-ω-hydroxyl-PS-b-PB (TIPS−O−PS−b−PB−OH) diblock copolymer.
3.3 Results and Discussion

Figure 3.8 Scheme illustrating the synthesis of LSBL’ asymmetric tetrablock terpolymer.

Size exclusion chromatography (SEC) performed on the TIPS–O–PS–b–PB–OH product (Figure 3.2) showed a monomodal and symmetric peak ($Đ = 1.05$). $^1$H NMR analysis provided clear evidence of the methylene units adjacent to the TIPS-protected α- (3.50 ppm) and unprotected ω-hydroxyl (3.65 ppm) end groups, while integrations of those peaks indicated that the PS–b–PB polymers were quantitatively functionalized at both ends (Fig. S1). The molecular weight and weight fractions of the diblock ($M_n = 12.0$ kDa, $f_s = 0.55, f_B = 0.45$ by $^1$H NMR spectroscopy) were calculated by comparing the integrations of the characteristic peaks of the PS and PB blocks with the integration of the TIPS group at 1.0 ppm. $^1$H NMR end group analysis also showed that the experimental molar mass was in agreement with the theoretical molar mass of polystyrene indicating quantitative conversion of styrene after 1 hour. Moreover, due to the use of TMEDA in a
three-fold excess compared to the anionic sites, the microstructure of the PB was ~76% 1,2-addition.

In the next step the freeze dried TIPS−O−PS-b-PB−OH was used as a macroinitiator for the polymerization of (±)-lactide in dichloromethane at room temperature. DBU was used as the catalyst, yielding the narrow dispersed triblock TIPS−O−PS-b-PB−b-PLA-OH (TIPS-O-SBL′′-OH) \((M_n = 20.6\text{ kDa}, \text{ weight fractions: } f_S = 0.32, f_B = 0.26, f_L = 0.42 \text{ by } ^1\text{H NMR, } D = 1.07 \text{ by SEC})\). One way to synthesize the desired tetrablock with asymmetric PLA end blocks is to cap the ω-hydroxyl end group of the TIPS-O-SBL′′-OH triblock, followed by the deprotection of the α-hydroxyl end group and subsequent LA polymerization from the α-position. However, the simplest way to get the same final product is to initially deprotect the α-hydroxyl end group to get the difunctional macroinitiator HO-SBL′′-OH and then simultaneously grow PLA from both ends. One way to synthesize the desired tetrablock with asymmetric PLA end blocks is to cap the ω-hydroxyl end group of the TIPS-O-SBL′′-OH triblock, followed by the deprotection of the α-hydroxyl end group and subsequent LA polymerization from the α-position. However, the simplest way to get the same final product is to initially deprotect the α-hydroxyl end group to get the difunctional macroinitiator HO-SBL′′-OH and then simultaneously grow PLA from both ends.198,199 The preexisting PLA block will ensure the asymmetrically sized PLA end blocks in the final product. Following the latter strategy, the TIPS-O-SBL′′-OH triblock was used as a substrate for the deprotection of the α-hydroxyl end group. However, by applying the usual agents found in the literature (TBAF, HCl) for the deprotection of the TIPS group, PLA degradation resulted as well. Modifications in the reaction conditions, reaction times, and concentration of the acidic or basic agents led either to PLA degradation or to non-quantitative TIPS cleavage. Efforts for buffering TBAF by the addition of CH₃COOH did not resolve the problem, while the use of alternative agents used in the literature in similar reactions was not fruitful. However, when a catalytic amount of Sc(OTf)₃ was used, complete removal of the TIPS group took place, while the PLA block remained intact. This result was evidenced both by ^1H NMR spectroscopy and SEC. The characteristic peak of TIPS at 1.0 ppm completely disappeared (Figure 3.3), while the SEC traces of TIPS-O-SBL′′-OH and HO-SBL′′-OH (Figure 3.2) were identical. In order for this reaction to take place, the presence of acetonitrile was necessary, while a two-day reaction time was required to ensure completion of the deprotection reaction. Sc(OTf)₃ has been used in the past as a catalyst for the ring opening polymerization of lactones and as a Lewis acid catalyst in
3.3 Results and Discussion

organic synthesis\textsuperscript{216,217} such as acylation,\textsuperscript{218,219} allylation,\textsuperscript{220} Diels-Alder\textsuperscript{221,222} and Fiedel-Craft\textsuperscript{223} reactions. There are also a few publications where Sc(OTf)\textsubscript{3} is used as a catalyst for the deprotection of silyloxy ethers.\textsuperscript{224,225} However, to the best of our knowledge, this is the first time that the use of Sc(OTf)\textsubscript{3} as an agent for the selective deprotection of the TIPS group in the presence of PLA is reported. In this reaction Sc(OTf)\textsubscript{3} can be used in catalytic amounts, it is compatible with PLA and is more suitable for the synthesis of sustainable polymers as it exhibits lower toxicity than TBAF, the usual agent for the deprotection of silyloxy ethers.

In the last step of the synthesis the HO-SBL’’-OH triblock was used as difunctional macroinitiator of LA. The usual reaction conditions were applied in order to yield the desired LSBL’ tetrablock ($M_n = 31.7$ kDa, weight fractions: $f_S = 0.21, f_B = 0.17, f_L = 0.18, f_{L'} = 0.44$ by $^1\text{H}$ NMR, $D = 1.12$ by SEC). The SEC trace of the final product is shown in Figure 3.2, while in Figure 3.3 the corresponding $^1\text{H}$ NMR spectrum is presented. It is worth noting that trace amounts of homopolymer and diblock impurities remain in the final product. The diblock impurities may result from non-quantitative chain initiation of TIPS-O-SB-OH while synthesizing TIPS-O-SBL”-OH. Additional impurities may have resulted from the polymerization of (±)-lactide by trace amounts of leftover methanol or PS-OH chains. In order to additionally prove that the final product has asymmetrically sized PLA end blocks, two control experiments were conducted. Firstly, a polystyrene homopolymer was synthesized by anionic polymerization using TIPSPrLi as an initiator, followed by termination with methanol (Scheme S1a). Then, the TIPS group was cleaved using Sc(OTf)\textsubscript{3}, followed by the polymerization of LA from the α-hydroxyl end group. The reaction conditions for these reactions were similar as in the tetrablock synthesis. As evidenced by the clear shift of the SEC trace (Figure 3.4) and the $^1\text{H}$ NMR analysis (Figure 3.5) the PS macroinitiator quantitatively initiated the polymerization of LA, indicating full functionality of the α-hydroxyl group after the Sc(OTf)\textsubscript{3} catalyzed TIPS deprotection. Along the same line, a second control experiment was conducted (scheme presented in Figure 3.9).
In this case, the TIPS-O-SBL’’-OH triblock was used as a LA macroinitiator. As evidenced by the SEC analysis (Figure 3.4), the trace of the product has shifted to lower retention times, which means that the ω-hydroxyl end group of the triblock precursor is fully functional. Thus, from the outcome of the two control experiments we concluded that both hydroxyl end groups are functional and that the route described above can lead to the synthesis of well-defined tetrablocks with asymmetric PLA end blocks.

3.3.2 Synthesis of SIOS’ asymmetric tetrablock terpolymers

The general reaction scheme used to synthesize the asymmetric tetrablock terpolymers is illustrated in Figure 3.10. A hydroxyl terminated poly(styrene)-b-poly(isoprene) (SI-OH) diblock was synthesized in cyclohexane at 40 °C by sequentially adding styrene and isoprene to sec-butyllithium initiator in an argon atmosphere. Subsequent addition of ethylene oxide results in the incorporation of a single –CH₂CH₂O- unit to the living chain due to the reduced nucleophilicity of the oxanionic species in the presence of lithium.
The diblock was terminated with acidic methanol and the SEC trace indicated a monomodal distribution with low dispersity ($D = 1.03$). Reinitiation of the purified diblock was accomplished by dissolving the polymer in tetrahydrofuran and titrating to the corresponding potassium alkoxide using potassium naphthalenide. With the oxanion nucleophilicity now increased in the presence of potassium counterions, addition of ethylene oxide allowed chain propagation. Subsequent termination with acidic methanol yields poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide) (SIO-OH) triblocks. Such a procedure is well-established and led to the synthesis of narrowly disperse SIO triblock terpolymers ($D = 1.05$).

Starting with the ABC triblock, two potential polymerization methods were considered for synthesizing the corresponding asymmetric ABCA' tetrablock: atom-transfer radical polymerization (ATRP) and radical addition-fragmentation chain-transfer polymerization (RAFT). However, the ATRP approach was discarded as polyisoprene has a tendency to chelate the copper catalyst rendering the polymerization ineffective. Thus, RAFT was approached as an alternate method due to its compatibility with a variety of monomers (including isoprene, styrene, and ethylene oxide) and reaction conditions. Transformation of the hydroxyl end group of poly(ethylene oxide) into thiocarbonylthio moieties by esterification using acid chloride or carboxyl functionalized thiocarbonylthio compounds has been widely reported. The procedure reported by Zhou et al. was used to attach the chain transfer agent (CTA) to the SIO-OH triblock by means of an acid chloride intermediate yielding the SIO-CTA macro chain transfer agent. This particular CTA (S-1-dodecyl- S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate) was chosen because it affords extremely high chain transfer efficiency and has been used to synthesized well-defined block copolymers containing polystyrene. In order to synthesize the CTA, a previously published procedure was followed with a few modifications made in order to increase the yield of the reaction and reduce the steps needed to isolate and purify the final product (see experimental section for details). For this purpose, no phase transfer catalyst was used. All reagents were mixed together, followed by titration with the potassium hydroxide solution. Quick stirring ensured
mixing of the components. After stirring overnight and neutralization of the reaction mixture, the acetone was rotovapped leading to product precipitation. The latter was isolated by simple filtration and purified by recrystallization in hexanes. After the reaction of SIO-OH with CTA and thorough purification, SEC analysis of SIO-CTA triblocks showed no change in molar mass distribution (Figure 3.6). $^1$H-NMR experiments indicated the integrations of peaks e and f (which correspond to the two protons next to the carboxyl and thiocarbonylthio groups, respectively) were similar (Figure 3.7), indicating the reaction was quantitative and all unreacted CTA had been removed.

Lastly, the parameters associated with RAFT polymerization were optimized in order to synthesize a tetrablock with the desired block lengths and qualities appropriate for phase behavior studies. Specifically, the final polymer should be of targeted composition and nearly monodisperse ($D < 1.1$) since dispersity has been shown to have an effect on
polymer phase behavior. Initial experiments were driven by polymerization conditions shown in previous literature on the RAFT polymerization of styrene and the procedure was subsequently optimized. To maintain low dispersity in polymer products, it is necessary to minimize the fraction of initiator derived chains. Previous literature values state $[CTA]:[AIBN] = 10:1$ is an optimum ratio that minimizes homopolymer impurities, using this ratio yielded tetrablocks of low dispersity. RAFT polymerizations were tested in bulk and in solution with toluene, benzene, and anisole. Reactions in bulk yielded high conversion even at low times (~2 hours) but resulted in polymers of high dispersity ($D > 1.3$). Reactions performed in anisole and benzene at 80 °C for 8 hours yielded low conversions (<15%) and moderate to high dispersities (1.12 and 1.27, respectively). In contrast, polymerizations carried out in toluene at the same reaction conditions consistently yielded well-defined polymers with $D \leq 1.1$ and conversions above 20%. SEC traces of reactions that were allowed to proceed for much longer than 8 hours displayed a shoulder at high molecular weights indicating that a significant amount of chain termination events were occurring by coupling. Additionally, following the literature, the reaction was performed in 50% v/v solvent to monomer. Thus, using these optimized conditions, well defined asymmetric SIOS’ polymer were polymerized with narrow dispersity and specified compositions ($M_n = 42.7$ kDa, $f_S = 0.11, f_I = 0.22, f_O = 0.27, f_{S'} = 0.40$ by $^1$H-NMR, $D = 1.08$ by SEC). Here, $M_n$ represents the number-average molecular weight and $f_A$ represents the weight fraction of monomer A; all compositions were within 10% of specified goals. SEC traces during each step of the reaction indicate the increase in molecular weight after the addition of each block (Figure 3.6). However, trace amounts of terminated polystyrene homopolymer chains can be seen in the final product. $^1$H NMR experiments also show the appearance of peaks corresponding to the growth of styrene, isoprene, and ethylene oxide blocks (Figure 3.7).

3.4 Conclusions

The two different strategies presented in this chapter offer the opportunity to synthesize a wide variety of well-defined multiblock polymers with tunable block sizes.
3.4 Conclusions

The synthetic routes include combinations of anionic polymerization with RAFT or ROP. These different polymerization methods allow the synthesis of block polymers with many different possible block types and lengths, while post polymerization reactions further extend the capabilities of these strategies, allowing the generation of specific structures among a plethora of possible combinations in order to target for specific material properties. In addition to sequential polymerization\textsuperscript{185}, coupling chemistry\textsuperscript{140}, and reinitiation of telechelic BC diblocks\textsuperscript{162}, the strategies reported within this paper add to the growing toolkit of synthetic routes capable of producing both symmetric and asymmetric ABCA tetrablocks, giving access to a wider array of monomers and, therefore, potential applications.
Chapter 4

Influence of Molecular Symmetry and Non-Ergodicity on the Phase Behavior of ABAC-Type Tetrablocks*

4.1 Introduction

Block polymers are macromolecules that contain discrete sequences of chemically distinct repeat units that can segregate into periodic nanoscale structures containing various domain geometries. The simplest molecular architecture in this class of self-assembling materials is the AB diblock copolymer, which has been extensively studied. In his seminal 1980 publication, Leibler developed a mean-field theory of phase equilibria in AB diblocks based on just two parameters: the product $\chi_{AB}N$, termed the segregation strength, and $f_A$, the volume fraction of block A. The domain geometry and ordered state symmetry are controlled primarily by $f_A$ when $\chi_{AB}N >> 10$, denoted strong segregation, whereas the order-disorder transition (ODT) boundary depends on both parameters. Only three ordered phases were found to be stable near the ODT: one-dimensional lamellae (LAM), two-dimensional hexagonally ordered cylinders (HEX$_C$),

* Adapted with permission from Chanpuriya, S.; Kim, Kyungtae; Zhang, Jingwen; Lee, Sangwoo; Arora, Akash; Dorfman, Kevin D.; Delaney, Kris T.; Fredrickson, Glenn H., and Bates, Frank S. ACS Nano, 2016, 10, 4961–4972. Copyright 2016 Chemical Society
and a three-dimensional body-centered cubic (BCC) arrangement of spheres. Subsequent experiments confirmed the now ubiquitous sphere-forming BCC phase in many diblock copolymer systems. We note that, while these domains are frequently referred to as spheres, they are actually soft polyhedral particles with facets dictated by the lattice symmetry and the necessity to fill space at uniform density; for simplicity we refer to the morphology as spherical. Subsequent refinements of Leibler’s treatment based on the framework of self-consistent field theory (SCFT) have accounted for additional phases in diblocks (e.g., Gyroid and O), and a rich assortment of morphologies in triblock terpolymers and higher functionality multiblocks. In many cases, these theoretical developments have been motivated by experimental findings driving subsequent expanded synthetic and structural characterization efforts that lead to additional insights. Recent discovery of the complex low symmetry Frank-Kasper $\sigma$ phase in an asymmetric diblock copolymer spawned another such cycle, where Xie et al. identified conformational asymmetry as a key ingredient for stabilizing this fascinating quasicrystal approximant.

Advances in polymer synthetic chemistry have opened virtually unbounded vistas for creating multiblock polymers with nearly unrestricted design flexibility. Increasing the number of blocks and the diversity of block chemistries leads to a rapid escalation in the degrees of freedom, even when restricted to linear, single-component block polymers. For example, a tetrablock molecular architecture built from three different repeat units affords access to nine distinct block sequences (ABAC, ABCA, ACAB, etc.) each offering independent control over the block molecular weights and hence composition. Selection of the block chemistries sets the three (temperature dependent) segment-segment interaction parameters ($\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$) that control the segregation strength. Clearly, the paradigm of experimentally driven theory needs to be inverted in order to exploit the remarkable opportunities for materials design afforded by polymer science and engineering. This chapter describes a recent collaboration, driven by the Materials Genome Initiative (MGI), to accomplish this goal.
Poly(styrene)-b-poly(isoprene)-b-poly(styrene)',b-poly(ethylene oxide) (SIS'O) tetrablock terpolymers were selected as an exceptional target opportunity. This type of multiblock has been shown to produce several intriguing morphologies in the limit of a minority of O and equal size S blocks, including the σ and dodecagonal quasicrystal (DDQC) phases. We identified the molecular symmetry parameter $\tau = N_S/(N_S + N_S')$ as a prime candidate for investigation. SCFT calculations indicated that the window of sphere forming morphologies was highly sensitive to $\tau$ and anticipated new modes of ordering. Guided by these calculations, a series of eight SIS'O polymers were synthesized using anionic polymerization; Figure 4.1 depicts the molecular structure and the distribution of blocks in the core and corona of the associated domains. Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) experiments revealed an extraordinarily rich complement of packing symmetries, nine in total, as a function of temperature and $\tau$, reflecting both equilibrium and metastable states. These results indicate a transition from ergodic to non-ergodic behavior with the development of strong segregation as the temperature is lowered below the order-disorder transition temperature ($T_{ODT}$). We associate this transition, at a temperature denoted $T_{erg}$, with the rapid extinction of chain exchange (diffusion) as the temperature is reduced and the penalty for moving O blocks through the S'1S matrix increases dramatically. SCFT calculations suggest that repositioning of the S and I blocks influences the formation of metastable states when $T < T_{erg}$.

The findings and interpretations reported here provide important insights into several aspects of nanostructure formation in soft materials. Perhaps most significant is a demonstration of the power derived from directly coupling theory and experiment in the quest for efficient materials design. Identification of the remarkable impact of the molecular symmetry parameter $\tau$ reinforces the notion that multiblock copolymers offer unparalleled possibilities for creating precisely tailored morphologies. More broadly, we believe knowledge gained by understanding this class of matter will inform theory and simulation258–260, and experiments on other classes of self-assembling soft materials such as surfactants, lipids, hybrid nanoparticles, and dendrimers,86,270–272
and has the potential to provide a better fundamental understanding of the factors responsible for the formation of low symmetry phases and aperiodic quasicrystals in hard materials.\textsuperscript{82,85,88,148,273}

4.2 Methods

4.2.1 Synthesis

Figure 4.1a shows the molecular structure for the poly(styrene)-\textit{b}-poly(isoprene)-\textit{b}-poly(styrene)′-\textit{b}-poly(ethylene oxide) tetrablock terpolymers used in this study, which were prepared using a two-step anionic polymerization method. Details of the monomer and solvent purification, and polymerization procedure are described elsewhere.\textsuperscript{131,190,194} In the first step, styrene (S) polymerization was initiated by sec-butyllithium at 40 °C in cyclohexane under an argon atmosphere. Subsequently, carefully metered amounts of isoprene (I) and styrene were sequentially added to the reactor. Aliquots were taken before each monomer charge for size-exclusion chromatography (SEC) and proton nuclear magnetic resonance spectroscopy (\textsuperscript{1}H NMR). After completion of the SIS′ polymerization, a 10-fold molar excess of ethylene oxide (O), relative to sec-butyllithium, was added to the solution and allowed to react for 2 h. The reaction was terminated with excess degassed methanol yielding a hydroxyl end-capped poly(styrene)-\textit{b}-poly(isoprene)-\textit{b}-poly(styrene)′ (SIS′-OH) triblock. SIS′-OH was precipitated in methanol, decanted, filtered, and freeze-dried from benzene. In the second step, SIS′-OH
as reinitiated by reaction with potassium naphthalenide in tetrahydrofuran (THF) at 40 °C followed by the introduction of a carefully measured amount of O. The monomer was allowed to react for 48 h prior to termination with excess degassed methanol. This method provides for the facile synthesis of multiple tetrablocks containing different lengths of O from a single batch of SIS’-OH precursor; the synthetic route is illustrated in Figure 4.2. Excess THF was removed by rotary evaporation to yield a concentrated SIS'O polymer solution. Finally, the tetrablocks were precipitated in cold (-78 °C) isopropanol, decanted, and filtered. Then, 0.5 wt. % (relative to the tetrablock mass) of butylated hydroxytoluene (BHT) was added to the solution as an antioxidant, and the polymer was freeze-dried from benzene.

4.2.2 Molecular Characterization

The absolute number-average molecular weight of the first S block ($M_{n,S}$), and the molecular weight distributions and dispersity indices for SI, SIS' and SIS'O were obtained using size exclusion chromatography (SEC), operated with THF as the mobile phase and calibrated with polystyrene standards (Polymer Laboratories). The overall number-average molecular weight ($M_{n,SIS'O}$) was calculated using $M_{n,S}$ and the weight
4.2 Methods

Fractions determined using $^1$H NMR. NMR spectra were acquired with CDCl$_3$ as the solvent on a Varian VI-500 spectrometer and referenced to the residual solvent peak. The mole fractions of poly(styrene), poly(isoprene), and poly(ethylene oxide) blocks were quantified using the integrated area under well-defined resonances, and these values were subsequently converted to weight fractions. Volume fractions were obtained by using published homopolymer densities at 140 °C ($\rho_S = 0.969$ g/cm$^3$, $\rho_I = 0.830$ g/cm$^3$, $\rho_O = 1.064$ g/cm$^3$). All samples discussed here are referred to as SIS′O-τ, where $\tau = N_S/(N_S + N_S')$ in which $N_S$ and $N_S'$ are the degrees of polymerization of the terminal and interior poly(styrene) blocks, respectively. Representative SEC and $^1$H NMR traces are shown in Figures 4.3a and 4.4, respectively. Additionally, SEC traces obtained following the most severe thermal treatments ($T > 250$ °C for 2 hours) are shown in Figure 4.3b.

4.2.3. Small-Angle X-Ray Scattering (SAXS)

Synchrotron SAXS experiments were conducted at the DND-CAT 5-ID-D beamline at the Advanced Photon Source (Argonne National Laboratory, Argonne, IL), using $\lambda = 0.729$ Å wavelength X-rays and a sample-to-detector distance of approximately 8.5 m. 2D data were collected on a Rayonix area CCD detector and azimuthally averaged. SAXS results are reported as intensity vs. scattering wave vector magnitude $q = |\vec{q}| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$, where $\theta$ is the scattering angle. Specimens (10-20 mg) were hermetically sealed in aluminum DSC pans. Data from SIS'O-0.68 and SIS'O-0.73 (Table 4.1) were obtained by annealing the samples for 2-10 minutes at specific temperatures after rapidly heating (ca. 130 °C/min) from the freeze dried state. All other SIS'O samples were annealed at 120 °C in vacuum for one day then quenched in liquid nitrogen to preserve the morphology. At the beamline, these samples were rapidly reheated to specified temperatures and annealed for 5-10 minutes before acquiring a scattering pattern. Temperature was controlled within ±1 °C using a Linkam DSC stage. The SAXS data containing clearly delineated Bragg peaks were analyzed using conventional crystallographic methods.
Figure 4.3 (a) Representative SEC traces obtained from final SIS'O tetrablock and intermediate aliquots. (b) SEC trace of SIS'O-0.73 before and after exposure to temperatures above 250 °C for approximately 2 hours during the SAXS experiments.

Figure 4.4 Representative $^1$H NMR spectrum for final SIS'O tetrablocks. Protons corresponding to each relevant peak are labeled.
Table 4.1 Characterization data for reported SIS’O tetrablock terpolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kDa)$^a$</th>
<th>$M_n/M_n^b$</th>
<th>$f_S$</th>
<th>$f_I$</th>
<th>$f_O$</th>
<th>$\tau$</th>
<th>$T_{ODT}$ (°C)$^d$</th>
</tr>
</thead>
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<tr>
<td>SIS’O-0.21$^f$</td>
<td>19.7</td>
<td>1.04</td>
<td>0.40</td>
<td>0.44</td>
<td>0.16</td>
<td>0.21</td>
<td>&gt;250</td>
</tr>
<tr>
<td>SIS’O-0.32$^f$</td>
<td>19.1</td>
<td>1.07</td>
<td>0.48</td>
<td>0.46</td>
<td>0.07</td>
<td>0.32</td>
<td>153</td>
</tr>
<tr>
<td>SIS’O-0.39$^f$</td>
<td>17.0</td>
<td>1.04</td>
<td>0.46</td>
<td>0.47</td>
<td>0.07</td>
<td>0.39</td>
<td>130</td>
</tr>
<tr>
<td>SIS’O-0.50$^g$</td>
<td>23.0</td>
<td>1.04</td>
<td>0.46</td>
<td>0.46</td>
<td>0.08</td>
<td>0.50</td>
<td>196</td>
</tr>
<tr>
<td>SIS’O-0.61$^f$</td>
<td>24.2</td>
<td>1.05</td>
<td>0.45</td>
<td>0.46</td>
<td>0.09</td>
<td>0.61</td>
<td>177</td>
</tr>
<tr>
<td>SIS’O-0.68</td>
<td>21.5</td>
<td>1.04</td>
<td>0.43</td>
<td>0.43</td>
<td>0.14</td>
<td>0.68</td>
<td>285$^e$</td>
</tr>
<tr>
<td>SIS’O-0.70$^f$</td>
<td>20.7</td>
<td>1.14</td>
<td>0.43</td>
<td>0.45</td>
<td>0.12</td>
<td>0.70</td>
<td>177</td>
</tr>
<tr>
<td>SIS’O-0.73</td>
<td>22.4</td>
<td>1.03</td>
<td>0.42</td>
<td>0.45</td>
<td>0.13</td>
<td>0.73</td>
<td>284$^e$</td>
</tr>
</tbody>
</table>

$^a$Calculated using a combination of SEC and $^1$H NMR spectroscopy data. $^b$Determined through SEC. $^c$Volume fractions calculated from $^1$H NMR spectroscopy data using reported melt densities at 140 °C.$^{52}$ $^d$Obtained using DMS.$^e$Obtained using SAXS.$^f$Samples characterized by Dr. Jingwen Zhang.$^{53}$ $^g$Sample characterized by Dr. Bluemle and Dr. Lee.$^{22,61}$

4.2.4 Transmission Electron Microscopy

TEM data were obtained on Tecnai T12 and Tecnai G2 Spirit BioTWIN transmission electron microscopes operating at 120 keV at the University of Minnesota Characterization Facility. Samples were annealed in vacuum at specified temperatures then quenched in liquid nitrogen to preserve the melt state morphology. Thin slices (~50 nm) were obtained using either a Reichart or Leica UC6 ultramicrotome fitted with a Microstar diamond knife. Sections were collected on copper grids (Ted Pella) and stained using the vapor from a 2–4% aqueous OsO$_4$ solution for 10–15 minutes to obtain electron contrast; this reagent reacts preferentially with poly(isoprene) and renders I domains dark in the TEM images.

4.2.5 Dynamic Mechanical Spectroscopy

Linear DMS data were obtained using a Rheometric Scientific ARES strain-controlled rheometer fitted with 25 mm diameter parallel plates. All experiments were performed above the glass transition and melting temperatures of the PS and PEO blocks, respectively, ($T_{g,S} \approx 57$ °C, $T_{m,O} \approx 50$ °C as determined by DSC measurements). Samples
were prepared by compression molding the polymer powder into a 0.8 mm thick by 25 mm diameter disk at 150 °C under 2000 psi pressure for 5 minutes. Isothermal frequency sweep data were collected at select temperatures. Strain amplitude was set below the onset of nonlinearity as determined by strain sweeps between 0.1 and 10% at representative measurement temperatures.

4.2.6 Theoretical Calculations

Self-consistent field theory (SCFT) is among the most powerful tools to study the phase behavior of block polymers.\textsuperscript{30,32} The success of SCFT has been demonstrated previously in discovering new ordered structures\textsuperscript{36,275} as well as aiding in understanding the complex morphologies observed experimentally in block copolymers.\textsuperscript{37,276} SCFT is a mean-field theory that is strictly valid in the limit of infinitely long chains; as a result, it captures the order-disorder transitions only qualitatively, but predicts the relative stability of competing ordered phases with reasonable accuracy.

Although SCFT has been discussed previously,\textsuperscript{32,275,277,278} we provide a brief overview here to emphasize its important features. The SCFT framework is typically based on the standard Gaussian model, in which the polymer chains are treated as infinitely thin threads and their configurations are modeled using random-walk statistics.\textsuperscript{34} The local interactions driving de-mixing of dissimilar segments are modeled using are Flory-Huggins interaction parameters $\chi_{JK}$, while short-ranged hard-core repulsions are enforced by an incompressibility constraint.\textsuperscript{34} Within this description, the SCFT formalism results in a set of coupled non-linear equations that are solved numerically.\textsuperscript{277,278} Each self-consistent solution obtained in this way corresponds to a stable or metastable state which can be associated with a mesophase; a spatially periodic solution represents an ordered structure while a homogenous solution corresponds to the disordered phase. From such a solution, one can calculate relevant structural and thermodynamic quantities, such as free energy, domain spacing, and density profiles of different monomer types in the mesophase. In order to construct the phase diagram, the thermodynamically stable phase is determined by comparing the free energy of all competing mesophases. The inherent challenge in constructing the phase diagram is the need to know all the possible phases a
priori, so we restrict ourselves here by assuming that all the competing phases are already known.

The SCFT parameter space for the SIS’O tetrablock terpolymers involves five parameters: $\chi_{IS}, \chi_{SO}, \chi_{IO}, f_O$ and $f_I$, assuming the statistical segment lengths of all the monomer types are known. The degree of polymerization, $N$, is determined using the volume fractions and molecular weights of the different monomer types reported in experiments. We assume temperature independent statistical segment lengths $b_I = 0.60$ nm, $b_S = 0.54$ nm and $b_O = 0.78$ nm, for the PI, PS and PEO respectively, calculated for the common reference volume $v_{ref} = 0.118$ nm$^3$. The following effective binary interaction parameters were used ($T$ is in units of Kelvin):

\[
\chi_{IS} = \frac{26.4}{T} - 0.0287, \\
\chi_{IO} = \frac{180.0}{T} - 0.1158, \\
\chi_{SO} = \frac{35.8}{T} - 0.0275.
\]

These interaction parameters were obtained by adjusting the parameters published by Frienlinghaus et al.\textsuperscript{279} in order to best match the experimental order-disorder and order-order transitions reported by Bluemle et al.\textsuperscript{141} at 140 °C with mean-field theoretical predictions. We emphasize here that the choice of interaction parameters certainly affects the relative stability of different phases. However, we believe that these $\chi$ parameters provide a reasonable qualitative understanding for the chemically similar asymmetric SIS’O system.

4.3 Results

In order to examine the effect of asymmetry in length of S and S’, we begin with the calculation of phase boundaries as a function of the parameter $\tau$ at constant $f_S/f_I$, where $f_S$ accounts for both poly(styrene) blocks. Here, $\tau = N_S/(N_S + N_{S’})$ in which $N_S$ and $N_{S’}$ are the degrees of polymerization of the terminal and internal poly(styrene) blocks, respectively. Figure 4.5 shows the SCFT-computed phase boundaries for different
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**Figure 4.5** Order-disorder and order-order transitions for different values of the asymmetry, $\tau = \frac{N_S}{N_S + N_{S'}}$ from SCFT calculations at 180 °C. Results indicate the window for sphere-forming phases dramatically widens around $\tau = 0.7$, prompting experiments in this region of phase space. The calculations are done for $f_S/f_I = 0.93$ isopleth with parent SIS’ triblock molecular weight, $M_n = 20.8$ kDa that corresponds to $N = 298.5$. The degree of polymerization is obtained by using the reference volume, $v_{\text{ref}} = 118$ Å$^3$, and the densities reported at $T = 140$ °C.$^{52}$

asymmetry values in the range $0.2 < \tau < 0.9$. Here we are primarily interested in the phase behavior of (nominally) sphere-forming phases, so we omit the calculation of phase transitions for the non-sphere forming region. The calculations were done at $T = 180$ °C with the interaction parameters given in the methods section, and the degree of polymerization calculated using experimentally reported molecular weights and densities. Moreover, the calculation was done in a manner that mimics experiments: the volume fraction $f_O$ in Figure 4.5 corresponds to the amount of PEO added to a parent SIS’ triblock for the isopleth, $f_S/f_I = 0.93$.

The phase diagram in Figure 4.5 was constructed by considering face-centered cubic (FCC), body-centered cubic (BCC), hexagonally close packed (HCP), Frank-Kasper A15 (A15), and Frank-Kasper $\sigma$ ($\sigma$) phases as the competing sphere-forming morphologies along with the disordered and hexagonally packed cylinder (HEX$_C$) phases (see Figure 4.16 below for illustrations$^{280}$ of these phases). The triple points shown in Figure 4.5 were determined from a combination of estimating boundaries and bracketing where phases collapsed. We observed that the A15 phase is never the stable phase but competes with the $\sigma$ phase throughout the phase diagram with a difference in free energy of approximately $1 \times 10^{-3} k_BT$ per chain. Because of such a minute difference in the free energies, marginal changes in the interaction parameters might stabilize the A15 phase.
over the σ phase or may produce a triple point exhibiting a coexistence of A15 and σ with any of the other (BCC, FCC, HCP) sphere-forming phase. Nevertheless, Figure 4.5 demonstrates that the τ parameter has a significant effect on phase boundaries; an increase in τ widens the phase window for sphere-forming phases, providing room to enclose a host of different packing arrangements including the complex σ phase.

Motivated by these theoretical results, the experimental counterpart to this study focuses on the phase behavior of eight SIS′O samples with varying asymmetry in the lengths of the terminal and internal polystyrene blocks (denoted S and S′, respectively). This asymmetry, quantified by the τ parameter, is varied experimentally from 0.21 to 0.73, which includes the widest sphere forming region observed in the SCFT simulations around τ = 0.7. All SIS′-OH precursors fall approximately on the same $f_S/f_I = 1$ isopleth with the $f_O$ in subsequent tetrablocks being varied between 0.07 to 0.16. A detailed summary of molecular characterization for all samples is provided in Table 4.1. All samples discussed here are referred to as SIS′O-τ. Polymer morphology was mainly characterized using a combination of SAXS and TEM, above 100 °C and on specimens quenched from this temperature range to below the glass transition temperature, respectively. All measurements correspond to conditions well above the poly(styrene) glass transition; in all specimens $T_{g,SIS′} < 70$ °C due to mixing of the S and I blocks. The following paragraphs report the phase behavior observed in these samples as the asymmetry parameter τ was increased.

Throughout the temperature range of 100 – 250 °C for SIS′O-0.21 and 100 – 150 °C for SIS′O-0.32, the scattering patterns display peaks at $(q/q)^2 = 1, 3, 4$ with $q^*$ being the location of the primary peak (Figure 4.6a,b). These peaks are consistent with hexagonal ($P6mm$) symmetry. For SIS′O-0.32, above 150 °C the scattering pattern displays a single broad peak indicative of a state of disorder (Figure 4.6b). However, a surprising result is obtained from the TEM micrographs of this polymer: the microdomains are spherical instead of the expected cylinders and contain regions of 4- and 6-fold symmetry (Figure 4.6e). SIS′O-0.21 displays the same domain geometry as
4.3 Results

Figure 4.6 Representative SAXS patterns from (a) SIS’O-0.21 and (b) SIS’O-0.32 are consistent with reflections for hexagonal symmetry. TEM micrographs obtained from (c), (d) SIS’O-0.21 and (e) SIS’O-0.32 reveal the presence of spheres ordered on a lattice display four- and six-fold rotational symmetries.

Figure 4.7 (a) SAXS patterns obtained from SIS’O-0.39. Relative peak positions associated with hexagonal symmetry at 100 °C are labeled. The σ phase and disordered states are observed upon heating. TEM images obtained after annealing at (b) 100 °C (with Fourier transform) and (c) 120 °C. The morphology in (c) is consistent with the σ phase and the characteristic σ-element with 32.4.3.4 tiling is highlighted.
well (Figure 4.6c,d). These results parallel findings in another set of SISO tetrablocks on the $f_S/f_I = 2/3$ isopleth, where varying $f_O$ from 0.09 to 0.19 produced spherical microdomains on a lattice also consistent with hexagonal $P6mm$ space group symmetry. (Zhang and Bates interpreted the SAXS and TEM images, identical to those shown here for SIS'O-0.21 and SIS'O-0.32 as evidence for a simple hexagonal crystal structure with $P6/mmm$ symmetry.\cite{143} We now question that tentative interpretation and emphasize that the true crystallographic assignment for this morphology has not been definitively established.) This packing is referred to here as hexagonally packed spheres (HEXS) to avoid confusion with HCP or HEXC morphologies.

SAXS data for SIS'O-0.39 was collected in the 100 – 140 °C temperature range (Figure 4.7a). While heating, the sample shows reflections consistent with a HEXS assignment at 100 °C, further supported by large regions that exhibit 6-fold symmetry in TEM images (Figure 4.7b and inset Fourier transform). Although the TEM images reveal large grains of well-ordered spheres, peaks observed in the SAXS patterns are quite broad; this discrepancy most probably derives from a difference in annealing times for the SAXS (ca. 5 min.) and TEM (24 h) samples. Upon heating to 120 °C, the sample develops a scattering pattern consistent with that of the σ phase before disordering at 140 °C with the disappearance of all Bragg peaks. A representative TEM image obtained from a specimen annealed at 120 °C is shown in Figure 4.7c where the characteristic $3^2.4.3.4$ tiling of the σ phase is highlighted.

Adjusting the τ parameter to 0.5 results in a tetrablock containing symmetric interior and terminal poly(styrene) chain lengths; this sample was extensively characterized in previous publications (referred to as SISO-3).\cite{93,141} The associated core-shell particles display liquid-like packing (LLP) at lower temperatures and the σ phase between 140 – 224 °C before disordering at yet higher temperatures. A detailed structural understanding of the LLP state remains elusive but it seems to be characterized by regions of short-range correlated microdomain packing while lacking long-range order (a representative TEM image is shown below in Figure 4.9b). It is important to note that this state can be achieved either by heating from a freeze-dried state (as shown for SIS'O-0.50) or cooling...
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Figure 4.8 SAXS patterns obtained for SISO-11 show that (a) the LLP phase can be recovered upon quenching directly from the disordered state. If the DDQC phase is allowed to grow, it remains stable upon cooling and LLP is not recovered. (b) Comparison of the pattern observed in (bottom) SISO-11 to one obtained from (top) one triphenylene functionalized with benzyl ether and phenyl propyl ether dendrons which has already been identified as forming the DDQC (Adapted with permission from Percec et al. *JACS*, 2009, 131, 7662. Copyright 2009 American Chemical Society).281 Almost identical peak positions and intensities are observed between the two samples.

from the equilibrium disordered phase at a rate rapid enough to avoid ordering.

Experiments on another symmetric SISO tetrablock polymer described elsewhere282 show that the LLP phase is generated when the sample is quenched sufficiently far below $T_{ODT}$ (Figure 4.8a and see below).

Upon increasing $\tau$ further, the resulting SIS'O-0.61 and SIS'O-0.70 tetrablocks exhibit very similar behavior. From 120 to 160 °C, SAXS patterns for SIS'O-0.61 display two broad peaks indicating limited long-range structural order attributed to the LLP state (Figure 4.9a). At higher temperatures, SIS'O-0.61 has a SAXS pattern with three closely spaced strong peaks, along with a lower intensity peak at lower $q$, all centered around the same position where the $q^*$ peak dominates at lower temperature. These peak positions and relative intensity distributions are shown in Figure 4.8b to derive from a dodecagonal quasicrystal (DDQC).142,282 The same pattern is observed for SIS'O-0.70 from 140 – 150 °C (Figure 4.9b). Upon further heating to 170 °C for SIS'O-0.61 and 160 °C for SIS'O-
4.3 Results

Figure 4.9 SAXS patterns from (a) SIS’O-0.61 and (b) SIS’O-0.70 upon heating from a freeze-dried state. SIS’O-0.61 was annealed overnight at 120 °C and quenched in LN₂; the polymer exhibited broad peaks attributed to the LLP phase when heated back to 120 °C. Upon heating, patterns consistent with the DDQC and σ phases are observed before disordering. (c) TEM image obtained from SIS’O-0.61 annealed at 120 °C displays limited long-range order within the specimen with regions of short-range periodic order, consistent with LLP spheres. (d) Annealing at 170 °C for one day reveals a morphology consistent with the σ phase. Note that the phases seen here are also observed in SIS’O-0.73 when its temperature ramp is started from 260 °C. The morphology in (e), obtained from SIS’O-0.70 after annealing at 170 °C for one day is consistent with the σ phase.

0.70, the scattering pattern transforms into one characteristic of the σ phase. Both samples disorder around 180 °C (Figures 4.9a,b).

TEM analysis of SIS’O-0.61 at 120 °C led to micrographs showing limited long-range order in the specimen but with some degree of short range order, consistent with the LLP assignment (Figure 4.9c). Images acquired from SIS’O-0.70 at 170 °C contain tiling elements consistent with the σ phase (Figure 4.9e). Curiously, annealing SIS’O-0.70 at 140 °C for an extended period (24 h) reveals images inconsistent with any of the
Figure 4.10 (a) Unit cell and (b) structure model of the A15 phase tiling viewed along the [001] direction and corresponding simulated diffraction pattern (inset). (c) TEM micrograph obtained from SIS'O-0.70 tetrablock terpolymer after annealing for one day at 140 °C and corresponding FFT (inset). (d) Simulated density plots for O, I, S' (interior), and S (terminal) blocks in the xy-plane at z = 1/2 in the A15 phase of the SIS'O tetrablock terpolymer. The calculations are done at T = 180 °C, fO = 0.13 with parent triblock SIS' molecular weight, M = 20.8 kDa.

observed SAXS patterns (a representative micrograph is shown in Figure 4.10c). One candidate morphology consistent with these images is the A15 phase (space group \( Pm\bar{3}n \)), which has been experimentally reported in the proximity of the \( \sigma \) phase in several soft and hard materials including supramolecular dendrimers and transition metal alloys.\(^{84,283}\) Although the A15 phase has been anticipated in branched and conformationally asymmetric linear diblocks using SCFT simulations,\(^{37,284}\) these predictions have only been experimentally verified in branched diblocks\(^{285}\) to the best of our knowledge.

Figure 4.10 illustrates the unit cell of the A15 phase along with the corresponding tiling of the [001] projection. The tiling and its simulated diffraction pattern are strikingly similar to the TEM micrograph observed in the annealed SIS'O-0.70 samples and its Fourier transform. Appearance of the A15 phase, combined with the widening of the window for sphere forming phases from SCFT simulations, prompted a more detailed theoretical and experimental investigation of modestly asymmetric (\( \tau \approx 0.7 \)) SIS'O
tetrablock terpolymers. In order to elucidate the positions of each block in the SIS’O-0.73 tetrablock, density plots were generated for the A15 unit cell using SCFT results. Figure 4.10d depicts the density profiles of the O, I, interior S’, and terminal S blocks in the $xy$ plane sliced at $z = \frac{1}{2}$ of the A15 unit cell. The density profiles for the O and I blocks are intuitive and confirm that O forms the core while I fills the matrix. Unsurprisingly, the density plot for the interior S’ shows that this block mainly forms a shell to shield the O blocks from the I blocks, which are associated with the largest and most energetically unfavorable segment-segment interactions. However, some amount of terminal S is also present in the shell to further the shielding, while the rest fills the matrix along with I. Perhaps the most interesting observation in Figure 4.10d is that the matrix-forming I and terminal S blocks exhibit a moderate amount of segregation and a non-uniform spatial distribution that reflects the lattice symmetry.

As shown in Table 4.1, SIS’O-0.68 and SIS’O-0.73 are similar in O content and molecular symmetry to SIS’O-0.70. However, the relatively higher molecular weight of these two samples leads to higher (> 100 °C) order-disorder transition temperatures for these two samples than for SIS’O-0.70, which permits deeper quenches from $T_{ODT}$ before chain dynamics are impeded due to strong segregation (and eventually vitrification of polystyrene chains). Despite this advantage, polymer degradation is a concern at such high temperatures, especially due to the presence of poly(isoprene). SEC traces obtained following the most severe thermal treatments ($T > 250$ °C for 2 hours) demonstrate some broadening of the distribution of molecular weights (Figure 4.3b). Nevertheless, heating and cooling through $T_{ODT}$ did not affect the transition temperature as determined by SAXS and dynamic mechanical spectroscopy (DMS), indicative of limited impact of chain degradation.

Rheological measurements reveal that the SIS’ precursor remains disordered over the entire temperature range (85 °C – 285 °C) utilized in the scattering experiments (Figure 4.11). Scattering data on SIS’O-0.68 and SIS’O-0.73 show very similar behavior upon heating (Figure 4.12a,c). Heating a freeze-dried specimen of SIS’O-0.73 to 120 °C leads to three well-defined but relatively broad peaks at $(q/q^*)^2 = 1, 2, \text{ and } 5$. TEM analysis of
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Figure 4.11 Frequency sweep data collected at 85 °C and 1% strain for the SIS’ precursor to SIS’O-0.73. Scaling at low frequencies is close to terminal, confirming the sample is disordered at and above 85 °C.

this material annealed at 120 °C for 10 minutes reveals grains composed of spheres (particles) with periodic order. A FFT of these images displays “stretched” hexagons which is consistent with rhombohedral order and compatible with the observed SAXS peak ratios (Figures 4.13a,b). However, the assignment of a space group and detailed structural information cannot be addressed here due to an insufficient number of Bragg peaks. Additional experiments indicate that this structure is stable and largely recovered when cooling from any other temperature. Long term annealing leads to sharpening of the same peaks without the development of additional ones (Figure 4.13c)

Heating to 160 °C transforms the morphology to one consistent with an HCP phase (space group \(P6_3/mmc\)) as shown in Figure 4.12a; a detailed listing of peak assignment and associated lattice parameters are presented in Table A.1. Further heating to 240 °C leads to a scattering pattern that cannot be indexed based on any previously reported block copolymer morphology but is similar to those reported in thermotropic and lyotropic micelles for the A15 phase (space group \(Pm\bar{3}n\)).\(^{90,286}\) A detailed analysis of the diffraction data reveals quantitative agreement with an A15 assignment, as shown by the allowed reflections labeled in Figure 4.12a and listed in Table A.1. TEM micrographs obtained from SIS’O-0.73 annealed at 220 °C for 1 hour (Figure 4.14) compare favorably with a square tiling of the [001] projection of the A15 structure, and are consistent with
Figure 4.12 Synchrotron SAXS patterns at selected temperatures during (a) heating ramp (~1 °C/min) of SIS'O-0.73 starting at 120 °C. The tetrablock was freeze-dried from benzene and received no thermal treatment prior to the experiment. An unknown phase with possible rhombohedral symmetry (based on TEM experiments) is seen at 120 °C. Heating drives a transition to the HCP, A15, σ, and disordered phases. (b) SAXS patterns during a heating ramp starting at 260 °C for the same sample show different behavior. Patterns are consistent with the DDQC phase after a short anneal at 260 °C which transitions to σ at higher temperatures before disordering. (c) SAXS patterns collected during the heating ramp of SIS'O-0.68 from a freeze dried state. The heating ramp is started at 120 °C. During heating, the following sequence of phases is observed: rhombohedral \( \rightarrow \) HCP+HEX \( \rightarrow \) A15 \( \rightarrow \) σ \( \rightarrow \) DIS. This sequence is similar to the one observed for SIS'O-0.73. (d) SAXS patterns from SIS'O-0.68 upon cooling from the disordered phase. Reflections consistent with the BCC morphology are observed at 280 °C. An additional strong reflection is observed within the σ and HCP phases (labeled) indicating a mixture of phases upon cooling. The peak starts to disappear as the temperature is lowered further.
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Figure 4.13 (a) TEM images taken from SIS’O-0.73 annealed at 120 °C for 10 minutes and quenched using liquid nitrogen. The spheres formed by tetrablocks are apparent throughout the sample. FFT inset reveals a “stretched” hexagon indicating possible rhombohedral ordering within the sample. (b) Comparing SAXS patterns of a polymer sample annealed at 120 °C for 5 min vs 1 week reveals the emergence of sharp, Bragg-like peaks implying better ordering. However, based on the limited data, the identification of a specific space group is inconclusive.

Figure 4.14 (a) Structure model of the A15 phase tiling viewed along the [001] direction and (b) corresponding simulated diffraction pattern. (c) TEM micrograph obtained from SIS’O-0.73 tetrablock terpolymer after annealing for 1 hour minutes at 220 °C and corresponding FFT (inset) compare favorably to (a) and (b).
the TEM image from SIS'O-0.70 (Figure 4.10c). These real space TEM images combined with the reciprocal space SAXS patterns firmly establish the $Pm\bar{3}n$ space group and confirm the existence of the A15 phase within the SIS'O system at temperatures moderately below $T_{ODT}$. Heating SIS'O-0.73 further to 280 °C drives a transition to the $\sigma$ phase, a structure now well-established in both tetrablock and diblock copolymers (detailed structural information is presented in Table A.1).\textsuperscript{93,142} The sample disorders around 284 °C. SAXS experiments show that the same transitions are observed in SIS'O-0.68: $T_{Rhomb} < T_{HCP} < T_{A15} < T_{\sigma} < T_{DIS}$ (Figure 4.12c); detailed structural information for this sample is presented in Table A.2. Upon cooling from the disordered phase, the $\sigma$, HCP and rhombohedral (tentatively assigned) phases are recovered but the A15 phase is not seen (Figure 4.12d). SAXS traces also reveal that BCC order is briefly encountered close to $T_{ODT}$ as a transient phase before growth of $\sigma$ from the disordered phase (Figure 4.12d).

Strikingly different phase behavior was obtained from a freeze dried SIS'O-0.73 sample rapidly heated (~130 °C/min) to 260°C before subsequent heating through $T_{ODT}$ (Figure 4.12b). Upon reaching 260 °C, the sample produced broad peaks similar to those seen in SIS'O-0.61 corresponding to the LLP phase. Note that the same sample displays reflections consistent with the A15 phase when heated slowly to 260 °C from a starting temperature of 120 °C (Figure 4.12a). After annealing for five minutes, a characteristic set of 4 reflections develop, with a low intensity peak at lower $q$ adjacent to a triplet of higher intensity peaks. The same pattern is observed in SIS'O-0.61 at 160 °C, attributed to growth of the DDQC phase based on analogous scattering from DDQC forming dendrimers (see Figure 4.8b) and poly(isoprene)-$b$-poly(lactide) (IL) diblock copolymers as described elsewhere.\textsuperscript{92,281} Further heating to 280 °C and 180 °C for SIS'O-0.73 and SIS'O-0.61, respectively, drives a transition to the $\sigma$ phase before a single, broad peak is observed for both samples upon raising the temperature beyond $T_{ODT}$.

Additionally, annealing SIS'O-0.73 overnight at 140 °C reveals the presence of yet another phase not observed when the sample is heated to 140 °C from a freeze-dried state.
without annealing. SAXS patterns for the annealed sample indicate reflections consistent with a mixture of HCP and FCC morphologies as shown in Figure 4.15a. TEM analysis of SIS’O-0.73 samples annealed at 140 °C for three days reveals images consistent with the FCC structure (Figure 4.15c). FFT analysis of obtained images reveal $a_{TEM} = 29.6 \pm 3.8$ nm while $a_{SAXS} = 33.4$ nm. Close packed planes of either HCP or FCC exhibit 6-fold rotational symmetry and are indistinguishable in TEM images. Interestingly, these regions were rarely observed (not shown). The fascinating richness in the phase behavior of these SIS’O samples as a function of $\tau$ and thermal processing is summarized in Figure 4.16. While we have not exhausted all possible processing scenarios for this set of materials (for example, we overlooked cooling SIS’O-0.21, SIS’O-0.32, and SIS’O-0.39 from $T > T_{ODT}$ to confirm growth of the HEXS phase), the overall compliment of

Figure 4.15 (a) SAXS patterns obtained from SIS’O-0.73 annealed at 140 °C overnight and quenched in liquid nitrogen. Heating back to 140 °C at the start of the SAXS experiment reveals additional peaks inconsistent with HCP. Further heating causes the additional peaks to melt completely at 200 °C followed by growth of the A15 phase at 220 °C. (b) Detailed analysis of the pattern at 140 °C shows presence of additional peaks that can be indexed to the FCC morphology. (c) Tiling of the (100) FCC plane with unit cell (solid square) and the four-fold motif observed in corresponding TEM images (dashed square).
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Figure 4.16 Summary of morphologies observed in the SIS'O system at selected values of τ. Arrows indicate transitions documented experimentally upon heating and cooling. Transitions are reversible in the pseudo-diblock regime consistent with equilibrium, while the states identified in the transition and non-equilibrium regimes are path dependent.

Experimental and theoretical results reported here, and previously,\textsuperscript{93,141–143} provide a concrete basis for rationalizing the equilibrium and non-equilibrium phase behavior associated with asymmetric ABA'C type tetrablock terpolymers when $\chi_{AB} \equiv \chi_{AC} \ll \chi_{BC}$. 
4.4 Discussion

The most remarkable feature of the SIS'O phase behavior documented in the previous section is the cornucopia of morphologies afforded by this molecular architecture. As summarized in Figure 4.16, nine sphere forming ordered phases or states are observed within this system: HEXS, rhombohedral (tentative), HCP, FCC, A15, LLP, DDQC, σ, and BCC (transient), and disorder at elevated temperatures. Surprisingly, the BCC phase, which is observed frequently in single-component diblock melts, is seen only as a transient structure upon cooling high-τ samples from the disordered state (Figure 4.12d). SCFT simulations that motivated this study predict the presence of BCC and HEXC phases at lower τ values. Although simulations correctly anticipate hexagonal symmetry within that region of phase space, TEM images confirm the presence of spherical domains and the HEXS morphology. Absence of fluctuation effects in the mean-field formulation of SCFT combined with the use of a Gaussian chain model (which cannot account for finite-extensibility effects) may interfere with the ability of SCFT simulations to capture this spherical packing symmetry. First seen in symmetric SISO tetrablocks along the \( f_S/f_I = 2/3 \) isopleth, the presence of a HEXS morphology (space group \( P6_{3}mm \)) appears to be rare in soft materials although clearly this structure is rather prevalent in ABA'C type tetrablock polymers. The only other example of this symmetry that we are aware of is a reported columnar phase in certain dendrimers, where axial disorder along the [001] direction extinguishes \((hkl)\) reflections thus reducing scattering to the 2-dimensional \((hk)\) case. Alternatively, one of the many Frank-Kasper and Laves phases associated with tetrahedral particle coordination, some with highly extended c-axis unit cell dimensions, may be responsible for this behavior. We are currently exploring several candidate structures using SCFT methods.

Consistent with the qualitative predictions of the SCFT theory (Figure 4.5), increasing τ exposes a wide window of sphere-forming morphologies within the SIS'O system with rich phase behavior and several temperature dependent order-order transitions. Varying temperature also influences the nature of the local composition around the spherical cores, which contributes to the recorded particle packing symmetries. The particular
4.4 Discussion

sequencing of $\chi$ parameters, $\chi_{IO} \gg \chi_{SO} \approx \chi_{JS}$, drives formation of core-shell spheres at the compositions examined in this study.\textsuperscript{141} The molecular architecture mandates the presence of an S’ shell around the O core at all temperatures, which screens the most enthalpically costly O-I contacts at all temperatures below the mean-field limit, $T_{MF} \gg T_{ODT}$. Cooling towards and below $T_{ODT}$ from a high temperature increases block segregation. Near $T_{ODT}$ the continuous matrix of S and I blocks (and to a lesser extent S’ blocks) are relatively uniformly distributed in space around the O core. In this limit we believe the tetrablock terpolymer behaves like a pseudo diblock, [SIS’]-O, as depicted in Figures 4.17a and 4.17b. Moreover, in this regime the molecules can undergo chain exchange, allowing the system to equilibrate over experimentally accessible times, analogous to the behavior of IL diblocks that form the Frank-Kasper $\sigma$ phase within 20 to 30 $^\circ$C of $T_{ODT}$.\textsuperscript{82,287} With the exception of SIS’O-0.21 and SIS’O-0.32 (where the HEXS phase is adjacent to the disordered state) the $\sigma$ phase is obtained near $T_{ODT}$ upon heating from the freeze-dried state or cooling from the disordered state. This reversibility is consistent with our equilibrium argument. Absence of the $\sigma$ phase in the low-$\tau$ tetrablocks underscores the importance of the molecular symmetry in guiding the formation of specific equilibrium morphologies.

Cooling the pseudo-diblock strengthens segregation of O from [S’IS] and segregation of S from I in the coronas, thus reducing the rate of chain exchange (Figure 4.17c). Our recent investigation of IL diblocks has revealed that below a specific temperature, denoted $T_{erg}$, the supercooled disordered material becomes non-ergodic due to the catastrophic effects of restricted chain diffusion.\textsuperscript{287} (Here we note that the consequences of reducing the temperature below $T_{erg}$ should not be confused with the effects induced when approaching $T_g$ of the particle core, which also arrests chain exchange.\textsuperscript{82} In the present case, the O cores have a glass transition temperature ($T_{g,O}$) far below the temperatures accessed in the experiments). We believe that the thermal processing history dependence exhibited by the SIS’O materials at low temperatures reflects metastable states associated with restricted tetrablock diffusion when $T < T_{erg}$. Arresting chain exchange shifts the ordering mechanism to one dominated by S-I-S’ matrix
Figure 4.17 Schematic illustration of the hypothesized effect of temperature on the nature of SIS’O particles. (a) and (b) Close to $T_{ODT}$, the spheres possess a mobile core facilitating chain exchange and driving the formation of equilibrium disorder and σ phases. (c) However, below $T_{erg}$, stronger segregation between S and I arrests chain exchange immobilizing the core and leading to the formation of non-equilibrium morphologies.

segregation coincident with the appearance of non-equilibrium morphologies. Structure formation within this non-equilibrium regime is mediated by the matrix as mass exchange by overall chain diffusion and particle-level dynamics (e.g., translation, fusion, evaporation, etc.) are “frozen” out. Segregation of the I and S blocks within the matrix is supported by SCFT simulations as revealed by Figure 4.10d for the A15 phase in SIS’O-0.73 at 180 °C, approximately 100 °C below $T_{ODT}$. The confinement of the O and interior S’ blocks to the core and shell, respectively, is evident from the density distribution. Interestingly, the I and terminal S blocks still display significant mixing around 180 °C. However, cooling the material increases segregation within the S-I-S’ matrix which, in turn, may guide ordering of the spheres, leading to the formation of distinct domains for
each block and a different state of order for the particles. Importantly, at all measurement temperatures \((T \geq 120 \, ^\circ C)\) the blocks that make up the S’IS matrix are always far above the glass transition temperature \((T_{g,\text{matrix}} < 70 \, ^\circ C)\) due to the effects of mixing poly(isoprene) \((T_{g,I} = -70 \, ^\circ C)\) with poly(styrene) \((T_{g,S} = 100 \, ^\circ C)\). Thus, as the temperature is lowered, the HCP and (tentatively assigned) rhombohedral phases occur primarily as a consequence of increased spatial segregation between the I and S blocks. Both phases can be obtained by rapidly cooling from the pseudo-diblock regime or heating from a freeze-dried state. This matrix based metastable ordering obviates the sphericity arguments associated with the symmetry breaking that is speculated to produce the equilibrium Frank-Kasper \(\sigma\) phase. Thus, we hypothesize that ordering in the tetrablock terpolymer system can be categorized under two temperature dependent regimes: the chain exchange mediated pseudo-diblock regime and the non-equilibrium regime governed by matrix segregation. The latter is a direct consequence of the multiblock molecular architecture, which introduces additional internal degrees of freedom (not available to diblocks) with which to tailor the phase behavior of these nominally single component materials.

As demonstrated, the equilibrium morphologies associated with the pseudo-diblock regime can be obtained by heating from a freeze-dried state or cooling from the disordered state. Similarly, with the exception of the FCC state (which competes with HCP upon heating freeze dried SIS’O-0.73 to 140 \(^\circ C\); see Figure 4.15), phases in the non-equilibrium regime can also be obtained by heating from a freeze-dried state or cooling from the disordered phase (see Figure 4.16). However, within these two limiting regimes lies a transition zone comprised of metastable phases, including LLP, DDQC, and perhaps A15, whose formation is strongly path dependent. As Figure 4.12b illustrates, within SIS’O-0.73, the LLP state is only found when the sample is rapidly heated to 260 \(^\circ C\). The heating ramp from this starting temperature mirrors the results seen for SIS’O-0.61 (Figure 4.9a). In both samples, the LLP state is obtained by rapidly heating a sample from the freeze-dried state (or rapidly cooling SISO specimens from the disordered state; see Figure 4.8a). Subsequent heating renders the DDQC followed by the \(\sigma\) phase before disordering. The appearance of these phases parallels recent findings in poly(isoprene)-b-
poly(lactide) (IL) diblocks. The kinetically trapped LLP state is obtained in this diblock by quenching the disordered liquid rapidly enough and sufficiently far below \( T_{ODT} \) to avoid ordering (as opposed to heating from the freeze-dried state) which coincides with the results shown in Figure 4.8a for a SISO tetrablock. The LLP state likely contains some form of short-range polytetrahedral order, which eventually spawns the DDQC. Given enough time, the equilibrium \( \sigma \) phase is able to nucleate and grow through chain exchange and, perhaps, other particle-level relaxation processes.

When rapidly heated to 120 °C and 260 °C, freeze dried specimens of SIS'O-0.61 and SIS'O-0.73, respectively, evolve virtually identical phase behavior with subsequent heating. SIS'O-0.73 (and SIS'O-0.68) was designed to provide access to deeper quench depths. Frankly, we were surprised to discover that the LLP and DDQC phase could be accessed by rapid heating to a comparable temperature below \( T_{ODT} \). Even more surprising is the occurrence of the A15 phase at around 240 °C when SIS'O-0.73 is heated from 120 °C (Figure 4.12a). These experiments reveal a pronounced path dependence to the morphology, which we associate with the transition from ergodic to non-ergodic behavior. The A15 phase is observed only when heating from the HCP phase and does not appear when the sample is cooled from the \( \sigma \) or disordered phases. Upon heating, as chain exchange becomes a viable diffusion mode with decreasing segregation strength, the formation of A15 may facilitate a transition between the non-equilibrium HCP and equilibrium \( \sigma \) phases. The restriction of filling space at constant density necessitates distortions of the spherical tetrablock particles into distinct polyhedra of various shapes and sizes, i.e., Wigner-Seitz cells, as dictated by the lattice symmetry. The A15 lattice requires two different polyhedra and bridges the HCP phase, which requires only one polyhedron, to the \( \sigma \) phase, which requires five distinct polyhedral shapes and sizes for the particles. During the cooling experiment, matrix segregation guides the assembly of the particles, leading to formation of the HCP phase from the \( \sigma \) phase without an A15 intermediate. Additionally, SAXS patterns recorded by heating SIS'O-0.70 to 140 °C from a freeze-dried state indicate formation of the DDQC morphology within 5 minutes, while annealing the sample for one day at the same temperature reveals clear TEM
4.5 Conclusions

images of the A15 phase, suggesting this may be an equilibrium state at segregation strength slightly greater than that required to produce the σ phase (SCFT calculations on conformationally asymmetric diblocks anticipate this scenario). These experiments highlight the extraordinary sensitivity to small variations in molecular architecture and state properties along with the roles of metastability and path dependence in the formation of terpolymer morphologies. Despite the rich phase behavior already observed, the pronounced importance of path dependence also provides an opportunity to discover many additional phases within this system as the tetrablock is exposed to varying thermal treatments.

In some respects, the transition regime identified in Figure 4.16 may be the most intriguing part of the phase map shown. Here the effects of diffusion limitations are most pronounced, mediating the formation of specific phase symmetries, most remarkably the DDQC. At this point we cannot ascertain with certainty which phases exist in equilibrium at temperatures below those where the Frank-Kasper σ phase is clearly most stable. SCFT suggests that the sequence A15→σ→BCC→disorder should be observed with heating in conformationally asymmetric copolymers. Our theoretical calculations indicate extreme sensitivity to the precise assignment of the χ parameters, which have different temperature dependencies and composition dependence. This work provides unambiguous evidence as to the importance of combining quantitative theory (and simulation) with exacting polymer synthesis and precise structural characterization in pursuing the extraordinary opportunities presented by multiblock polymers.

4.5 Conclusions

Self-consistent field theory (SCFT) calculations combined with precise synthesis and quantitative structural characterization have revealed an extraordinary array of ordered states in sphere forming linear poly(styrene)-b-poly(isoprene)-b-poly(styrene)′-b-poly(ethylene oxide) (SIS′O) tetrablock terpolymers. A new molecular symmetry parameter, \( \tau = N_5/(N_5 + N_5′) \) in which \( N_5 \) and \( N_5′ \) are the degrees of polymerization of the terminal and interior poly(styrene) blocks, respectively, is shown to influence the formation of nine discrete states of order in this class of multiblock polymers.
4.5 Conclusions

Equilibrium and metastable morphologies are associated with temperature regimes near the order-disorder transition \( T_{ODT} \), and \( T \ll T_{ODT} \), reflecting the consequences of facile chain exchange and arrested molecular diffusion, respectively. We identify the transition between these two limits with cooling as a loss of ergodicity at a temperature denoted \( T_{\text{erg}} \) where diffusion limitations mediate the formation of the Frank-Kasper A15 phase, a hexagonal arrangement of spheres (HEXs), and a globally disordered state of liquid like packing (LLP) that spawns the dodecagonal quasicrystal (DDQC). At temperatures \( T \ll T_{\text{erg}} \) absence of chain exchange leads to ordering governed by the local spatial arrangement of the I and S (and to a lesser extent S’) blocks producing HCP, FCC, and rhombohedral (tentative assignment) order. This investigation demonstrates the importance of combining theory, computation, and experiments towards the discovery of new forms of self-assembled soft matter.
Chapter 5. Investigation of the HEKS Phase in Low-τ SIS'O Tetrablocks

5.1 Introduction

Investigations into the self-assembly of block polymers have been ongoing for about the past fifty years. Early experimental inquiries into sphere-forming block polymer phase behavior only revealed the presence of a body-centered cubic (BCC) phase\textsuperscript{58,61,62}, confirming Leibler’s theoretical predictions.\textsuperscript{30} In fact, the BCC phase remained synonymous with sphere-forming block polymer melts for a few decades.\textsuperscript{16,33} However, research interest in sphere-forming block polymers was reinvigorated recently, motivated by the simultaneous discovery of the Frank-Kasper $\sigma$ phase in poly(isoprene)-$b$-poly(lactide) (IL) diblocks and poly(styrene)-$b$-poly(isoprene)-$b$-poly(styrene)-$b$-poly(ethylene oxide) (SISO) tetrablocks.\textsuperscript{93} The parallels in phase behavior between these seemingly disparate molecular architectures were reinforced when a dodecagonal quasicrystalline (DDQC) morphology was found in both materials as well.\textsuperscript{92,142} Quasicrystalline order was seen to evolve out of a non-ergodic, liquid-like packing of spheres (LLP). Given enough time, the DDQC transitioned to the $\sigma$ phase; the dynamics of this transformation were strongly temperature dependent.\textsuperscript{282,287} Despite the fruitful collaboration between these polymers, tetrablock terpolymers have afforded access to a number of morphologies yet unseen in diblocks.\textsuperscript{289}
This variety in phase behavior seen in ABA′C-type tetrablocks derives from their unique molecular architecture. For example, tetrablock terpolymers afford access to a molecular symmetry parameter that has no analog in AB diblocks. This parameter $\tau$, defined as $\tau = \frac{N_A}{N_A + N_{A'}}$, has been shown to influence the phase boundaries and domain spacings in ABA triblocks. As $\tau$ deviates from $\frac{1}{2}$, part of one A segment is transferred from one block to another without stretching the molecule. Thus, asymmetric ABA′ (here, the prime symbol is used to signify molecular asymmetry) triblocks have a lower stretching energy in the A domain than the symmetric ABA-type triblock. If the asymmetry is sufficiently large, short A blocks can be pulled into the B domains. Extraction of the A block allows B chains to relax away from the interface without further stretching compensating for the enthalpic cost of A/B contacts. These subtle effects undoubtedly impact the phase behavior of SIS′O tetrablocks as shown in chapter 4. Only samples with low values of the symmetry parameter ($\tau \leq 0.3$) display simple hexagonal packing of spheres (HEXS).

The HEXS phase was first observed in symmetric SISO tetrablocks along the $f_S/f_I = 2/3$ isopleth in samples containing $0.09 \leq f_O \leq 0.19$. Small-angle X-ray scattering on these samples revealed diffraction patterns analogous to those of hexagonally packed cylinders (HEXC). Reflections were observed only at $(q/q^*)^2$ values of 1, 3, 4, and 7, where $q$ is the scattering wave vector and $q^*$ is the location of the primary peak. However, these results were quite surprising when combined with transmission electron microscopy (TEM) images which revealed the existence of spherical domains. Projections along different axes showed regions with 4- and 6-fold rotational symmetry. The unit cell proposed by Zhang et al. for this structure (space group $P6/mmm$) is illustrated in Figure 5.1. The reported scattering patterns captured the $(hk0)$ reflections consistent with the proposed placement of spherical domains within the hexagonal unit cell. However, additional peaks associated with $(hkl, l \neq 0)$ scattering were absent despite adjusting the lattice parameter ratio ($c/a$). This discrepancy was attributed to a lack of long-range order along the 6-fold axis relative to strong in-plane $(hk0)$ order. This axial disorder would result in a
columnar structure and extinguish $(hkl, l \neq 0)$ scattering, consistent with the observed scattering patterns.\textsuperscript{143}

Despite these insights, understanding of the HEX\textsubscript{S} phase remains incomplete. Particularly interesting are the origin of the hypothesized axial disorder and proximity of HEX\textsubscript{S} to the DDQC in certain tetrablock samples.\textsuperscript{142} Unlike the morphologies observed so far, this phase does not display any clear equivalents in block polymers or even other classes of self-assembled matter. However, a few intermetallic compounds (e.g., CaCu\textsubscript{5}) order with the proposed $P6/mmm$ symmetry.\textsuperscript{290} In soft matter, the only other example of this morphology, to the best of the authors knowledge, is a columnar phase in certain dendrimers\textsuperscript{281}, where axial disorder along the [001] direction eliminates $(hkl)$ reflections. The prevalence of the HEX\textsubscript{S} morphology in low-$\tau$ SIS'O tetrablocks presents a fantastic opportunity to further explore the details of this phase. The following sections report the synthesis of asymmetric SIS'O tetrablocks of $\tau \leq 0.33$ and their thermal and morphological characterization through complementary use of dynamic mechanical spectroscopy (DMS), SAXS, and TEM.
5.2 Methods

5.2.1 Synthesis

Figure 5.2 shows the molecular structure for the poly(styrene)-b-poly(isoprene)-b-poly(styrene)′-b-poly(ethylene oxide) (SIS′O) tetrablock terpolymers used in this study, which were prepared using a two-step anionic polymerization method. Details of the monomer and solvent purification, and polymerization procedure are described elsewhere. In the first step, styrene (S) polymerization was initiated by sec-butyllithium at 40 °C in cyclohexane under an argon atmosphere. Subsequently, carefully metered amounts of isoprene (I) and styrene were sequentially added to the reactor. Aliquots were taken before each monomer charge for size-exclusion chromatography (SEC) and proton nuclear magnetic resonance spectroscopy (1H NMR). After completion of the SIS′ polymerization, a 10-fold molar excess of ethylene oxide (O), relative to sec-butyllithium, was added to the solution and allowed to react for 2 h. The reaction was terminated with excess degassed methanol yielding a hydroxyl end-capped poly(styrene)-b-poly(isoprene)-b-poly(styrene)′ (SIS′-OH) triblock. SIS′-OH was precipitated in methanol, decanted, filtered, and freeze-dried from benzene. In the second step, SIS′-OH was reinitiated by reaction with potassium naphthalenide in tetrahydrofuran (THF) at 40 °C followed by the introduction of a carefully measured amount of O. The monomer was allowed to react for 24 h prior to termination with excess degassed methanol. This method provides for the facile synthesis of multiple tetrablocks containing different lengths of O from a single batch of SIS′-OH precursor; the synthetic route is illustrated in Figure 5.3. Excess THF was removed by rotary evaporation to yield a concentrated SIS′O
polymer solution. Finally, the tetrablocks were precipitated in cold (-78 °C) methanol, decanted, and filtered. Then, 0.5 wt. % (relative to the tetrablock mass) of butylated hydroxytoluene (BHT) was added to the solution as an antioxidant, and the polymer was freeze-dried from benzene.

5.2.2 Molecular Characterization

The absolute number-average molecular weight of the first S block ($M_n,S$), and the molecular weight distributions and dispersity indices for SI, SIS’, and SIS’O were obtained using size exclusion chromatography (SEC), operated with THF as the mobile phase and calibrated with polystyrene standards (Polymer Laboratories). The overall number-average molecular weight ($M_{n,SIS'O}$) was calculated using $M_{n,S}$ and the weight fractions determined using $^1$H NMR. NMR spectra were acquired with CDCl$_3$ as the solvent on a Varian VI-500 spectrometer and referenced to the residual solvent peak. The mole fractions of poly(styrene), poly(isoprene), and poly(ethylene oxide) blocks were quantified using the integrated area under well-defined resonances, and these values were subsequently converted to weight fractions. Volume fractions were obtained by using
published homopolymer densities at 140 °C ($\rho_S = 0.969 \text{ g/cm}^3$, $\rho_I = 0.830 \text{ g/cm}^3$, $\rho_O = 1.064 \text{ g/cm}^3$). All samples discussed here are referred to as SIS'$_\tau$O-f$_O$, where $\tau = N_S/(N_S + N_S')$ in which $N_S$ and $N_S'$ are the degrees of polymerization of the terminal and interior poly(styrene) blocks, respectively, and $f_O$ is the volume percent of ethylene oxide within the tetrablock. Representative SEC and $^1$H NMR traces are shown in Figures 5.4 and 5.5, respectively.

5.2.3. Small-Angle X-Ray Scattering (SAXS)

Synchrotron SAXS experiments were conducted at the DND-CAT 5-ID-D beamline at the Advanced Photon Source (Argonne National Laboratory, Argonne, IL), using $\lambda = 0.729 \text{ Å}$ wavelength X-rays and a sample-to-detector distance of approximately 8.5 m. 2D data were collected on a Rayonix area CCD detector and azimuthally averaged. SAXS results are reported as intensity vs. scattering wave vector magnitude $q = |\vec{q}| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$, where $\theta$ is the scattering angle. Specimens (10-20 mg) were hermetically sealed in aluminum DSC pans. SAXS data were obtained by annealing the samples for 2-10 minutes at specific temperatures after rapidly heating (ca. 130 °C/min) from the freeze-dried state. Some samples received extended annealing times, as described in the results section. Temperature was controlled within ±1 °C using a Linkam DSC stage. The SAXS data containing clearly delineated Bragg peaks were analyzed using conventional crystallographic methods.

5.2.4 Transmission Electron Microscopy

TEM data were obtained on a Tecnai G2 Spirit BioTWIN transmission electron microscopes operating at 120 keV at the University of Minnesota Characterization Facility. Samples were annealed in vacuum at specified temperatures then quenched in liquid nitrogen to preserve the melt state morphology. Thin slices (~50 nm) were obtained using a Leica UC6 ultramicrotome fitted with a Microstar diamond knife. Sections were collected on copper grids (Ted Pella) and stained using the vapor from a 2% aqueous OsO$_4$ solution for 15 minutes to obtain electron contrast; this reagent reacts preferentially with poly(isoprene) and renders I domains dark in the TEM images.
5.2 Methods

Figure 5.4 Representative SEC traces obtained from final SIS'O tetrablock and intermediate aliquots. Peaks at high retention times result from impurities in the column and not terminated chains.

Figure 5.5 Representative $^1$H NMR spectrum for final SIS'O tetrablocks. Protons corresponding to each relevant peak are labeled.
5.2 Methods

5.2.5 Dynamic Mechanical Spectroscopy

Linear DMS data were obtained using a Rheometric Scientific ARES strain-controlled rheometer fitted with 25 mm diameter parallel plates. All experiments were performed above the glass transition and melting temperatures of the PS and PEO blocks, respectively, as determined by DSC measurements. Samples were prepared by compression molding the polymer powder into a 0.8 mm thick by 25 mm diameter disk at 150 °C under 2000 psi pressure for 5 minutes. Isochronal (1 rad/s) temperature ramp tests were performed at a strain amplitude of 1% at 2 °C/min. Isothermal frequency sweep data were collected at select temperatures. Strain amplitude was set below the onset of nonlinearity as determined by strain sweeps between 0.1 and 10% at representative measurement temperatures.

5.2.6 Differential scanning calorimetry

DSC experiments were conducted on a TA instruments Q1000 DSC. 5-10 mg of polymer was heated to 150 °C (well above the $T_g$ of S) to minimize the effects of prior thermal history. The sample was then cooled to -100 °C at 10 °C/min and data were collected during the second heating cycle, also at 10 °C/min. The degree of crystallinity of the PEO block was determined by normalizing the integrated melting peak to the bulk heat of fusion of PEO (213 J/g) as $X_c = \frac{\Delta H_m}{w_{PEO} \Delta H_{PEO, bulk}}$.
5.3 Results

In order to further probe the HEXS phase, tetrablocks of low \( \tau \) (\( \tau \leq 0.33 \)) were synthesized since these asymmetries have been shown to stabilize the HEXS phase.\textsuperscript{282,289} Two series of tetrablocks with different \( \tau \) values were synthesized and the molecular details are summarized in Table 5.1. Morphological characterization was carried out through complementary use of SAXS and TEM and found the existence of HEXS, BCC, \( \sigma \), LLP, and DDQC morphologies. These results are supported by thermal characterization through DSC and DMS, as detailed in the following sections.

Table 5.1 Molecular and thermal characterization data for SIS\(_{0.18}\), SIS\(_{0.33}\), and respective tetrablocks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( f_s^a )</th>
<th>( f_l^a )</th>
<th>( f_o^a )</th>
<th>( M_n ) (kDa)\textsuperscript{b}</th>
<th>( D )</th>
<th>( T_{\text{ODT}} ) (°C)\textsuperscript{c}</th>
<th>( X_e^d )</th>
<th>( T_{m,O} ) (°C)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS(_{0.18})</td>
<td>0.53</td>
<td>0.47</td>
<td>-</td>
<td>16.7</td>
<td>1.03</td>
<td>&lt;100\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIS(_{0.18})O-11</td>
<td>0.47</td>
<td>0.42</td>
<td>0.11</td>
<td>19.1</td>
<td>1.05</td>
<td>212</td>
<td>0.34</td>
<td>32</td>
</tr>
<tr>
<td>SIS(_{0.18})O-16</td>
<td>0.45</td>
<td>0.39</td>
<td>0.16</td>
<td>20.3</td>
<td>1.04</td>
<td>265</td>
<td>0.53</td>
<td>44</td>
</tr>
<tr>
<td>SIS(_{0.33})</td>
<td>0.52</td>
<td>0.48</td>
<td>-</td>
<td>17.4</td>
<td>1.03</td>
<td>&lt;100\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIS(_{0.33})O-04</td>
<td>0.50</td>
<td>0.46</td>
<td>0.04</td>
<td>18.2</td>
<td>1.04</td>
<td>&lt;100\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIS(_{0.33})O-06</td>
<td>0.49</td>
<td>0.45</td>
<td>0.06</td>
<td>18.7</td>
<td>1.04</td>
<td>&lt;100\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIS(_{0.33})O-09</td>
<td>0.47</td>
<td>0.44</td>
<td>0.09</td>
<td>19.5</td>
<td>1.04</td>
<td>200\textsuperscript{e}</td>
<td>0.41</td>
<td>38</td>
</tr>
<tr>
<td>SIS(_{0.33})O-11</td>
<td>0.46</td>
<td>0.43</td>
<td>0.11</td>
<td>19.9</td>
<td>1.04</td>
<td>180</td>
<td>0.28</td>
<td>38</td>
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<tr>
<td>SIS(_{0.33})O-14</td>
<td>0.45</td>
<td>0.41</td>
<td>0.14</td>
<td>20.8</td>
<td>1.04</td>
<td>219</td>
<td>0.55</td>
<td>42</td>
</tr>
<tr>
<td>SIS(_{0.33})O-15</td>
<td>0.44</td>
<td>0.41</td>
<td>0.15</td>
<td>21.1</td>
<td>1.04</td>
<td>244</td>
<td>0.61</td>
<td>44</td>
</tr>
</tbody>
</table>

\( ^a \)Volume fractions obtained from \(^1\)H NMR. \( ^b \)\( M_n \) obtained through a combination of SEC and \(^1\)H NMR. \( ^c \)\( T_{\text{ODT}} \) estimated from rheological temperature ramps. \( ^d \)Obtained using DSC. \( ^e \)Obtained used SAXS.
5.3 Results

5.3.1 SIS'0.18 and corresponding SIS'0.18O tetrablocks

DSC measurements (Table 5.1, Figure 5.6) display melting temperatures that increase with increasing $f_0$. Significant increase in percent crystallinity as O is added suggests at least partial segregation of domains. However, the level of crystallinity is slightly lower than those reported by Bluemle et al. in sphere-forming SISO polymers possibly due to the reduced molecular weight.\textsuperscript{141} Temperature ramp experiments conducted on both
SIS′$_{0.18}$O-11 and SIS′$_{0.18}$O-16 revealed order-disorder transitions at 212 °C and 265 °C, respectively. Frequency sweeps were used to further characterize viscoelastic behavior and revealed decidedly nonterminal behavior between 100 °C ≤ $T$ ≤ 200 °C, consistent with an ordered morphology (Figure 5.7a). $G''$ displays a distinctive dip at intermediate frequencies associated with triply periodic phases but $G'$ is seen to vary with frequency. Therefore, determination of the presence of a triply periodic versus cylindrical morphology is inconclusive based on this data alone.

SAXS pattern indicate that the triblock precursor (SIS′$_{0.18}$) remains disordered over the relevant temperature range ($T$ ≥ 100 °C). The ordered state symmetry of tetrablock samples was characterized through SAXS. Patterns collected for SIS′$_{0.18}$O-11 between 100 °C and the disordered state displayed reflections at $q/q^* = \sqrt{1}, \sqrt{3}, \sqrt{4}$ for any temperature, consistent with hexagonal symmetry. Importantly, cooling the sample from the disordered state produced the same reflections strengthening the claim that the observed phase may be an equilibrium structure (Figure 5.7b). 2D patterns obtained upon cooling SIS′$_{0.18}$O-11 through $T_{ODT}$ were initially coarse and anisotropic indicating the formation of large grains but transitioned to uniform rings as temperature was lowered further. Similar patterns were observed for SIS′$_{0.18}$O-16 upon heating and cooling (Figure 5.7c).

TEM images were produced from SIS′$_{0.18}$O-16 annealed for 1 day at 170 °C after cooling from disorder and used to elucidate the domain morphology. The presence of particles possessing six-fold symmetry (Figure 5.8a-c) is clear but arrangements with four-fold rotational symmetry are not observed. This observation is consistent with the previous report that asserts four-fold projections are relatively rare. Still, the absence of these projections is disconcerting and additional analysis was performed to confirm the presence of spherical rather than cylindrical domains. Firstly, FFT analysis of domains which appear to be cylindrical revealed an underlying periodicity along other directions (Figure 5.8d). Secondly, planar cuts at an oblique angle to the six-fold axis of HEXC...
Figure 5.7 (a) Frequency sweep data for SIS$_{0.18}$O-11 is consistent with an ordered morphology. However, determination of a two-dimensional or triply periodic morphology is inconclusive. SAXS patterns for (b) SIS$_{0.18}$O-11 and (c) SIS$_{0.18}$O-16 during heating and cooling ramps display reflections consistent with the HEX$_5$ phase.
5.3 Results

Figure 5.8 TEM micrographs from SIS′0.18O-16 annealed at 170 °C for one day display many regions of (a), (b), (c) six-fold rotational symmetry. (d) Domains which appear cylindrical contain modulations consistent with hexagonal symmetry as revealed by the FFT, consistent with the assignment of HEXS.

should produce elliptical or elongated O domains which were not observed in any of the images. Based on these results, both samples are assigned the HEXS morphology.

Despite the lack of TEM evidence for SIS′0.18O-11, it is rational to eliminate the presence of HEXC given the lower $f_O$. It is possible that a variety of other sphere-forming phases can be found if the SIS′0.18 series is explored more, allowing the development of structural relationships between different observed morphologies and further elucidating
the framework of the HEXS phase. However, based on these results (which display only
HEXS), synthetic efforts were focused on producing tetrablocks with a slightly higher
value of τ.

5.3.2 SIS′0.33 and corresponding SIS′0.33O tetrablocks

SIS′0.33O tetrablocks reveal a rich assortment of structured states including LLP,
DDQC, σ, HEXS, and BCC. The molecular and thermal characterization data for this
series is provided in Table 5.1. DSC data (Table 5.1, Figure 5.6) indicates at least partial
segregation of S and O domain with increasing fraction of crystalline domains as fO is
increased. Scattering experiments indicate a state of disorder for SIS′0.33, SIS′0.33O-02,
and SIS′0.33O-04 at and above 100 °C. The following paragraphs summarize
characterization results for tetrablocks of higher fO.

SIS′0.33O-09. Isochronal temperature ramps performed at 1 rad/s, 1% strain, and 2
°C/min on this sample displayed a precipitous drop in G′ at 159 °C, indicative of the
ODT(Figure 5.9a). This data was reinforced by terminal behavior (G′ ∝ ω^2, G′′ ∝ ω^1) seen
in frequency sweeps from 0.1 ≤ ω ≤ 100 rad/s at 160 °C (Figure 5.9b). However, SAXS
experiments performed at a similar heating rate do not show an ODT until at least 190
°C. Both experiments were carried out twice to ensure reproducibility at similar heating
rates (2 - 4 °C/min) and still yielded a large disparity of about 30 °C in observed ODTs.
Here, T_{ODT}s obtained from SAXS measurements are reported.

Below the ODT, morphological behavior was characterized through SAXS (Figure
5.9c) and yielded patterns consistent with LLP when the freeze-dried sample was heated
to 100 °C. As the sample was heated further, DDQC was observed starting at 170 °C. To
ensure consistency with previous experiments,92 the sample was also annealed for an
extended time (three days) at 120 °C. SAXS patterns from the annealed sample yielded
reflections compatible with the DDQC (not shown). Upon further heating, reflections
consistent with σ and BCC were observed at 180 and 190 °C, respectively. While order in
the σ phase is relatively poor (possibly due to insufficient annealing time), the pattern
displays additional peaks which cannot be indexed to the quasicrystalline structure. The σ
Figure 5.9 (a) Temperature ramp and (b) frequency sweep data indicate $\text{SIS}^{0.19}\text{O-11}$ is disordered by 160 °C. (c) SAXS patterns during heating and cooling ramps from $\text{SIS}^{0.33}\text{O-09}$ display formation of LLP, DDQC, $\sigma$, and BCC phases upon heating. The BCC and $\sigma$ phases are recovered upon slow cooling while the DDQC and LLP are not observed. The disordered phase is not observed until 200 °C.

phase was indexed as in Chapter 4 while indexing for the DDQC was performed following the procedures generated by Ishimasa et al. and Gillard et al. Cooling the sample from the disordered phase yields the BCC morphology. As peak intensities corresponding to BCC decrease upon further cooling, reflections consistent with the $\sigma$ phase appear, as expected. The $\sigma$ phase is initially poorly ordered but displays additional allowed reflections upon annealing for one week at 120 °C (Figure 5.9c). The LLP and DDQC phases are not seen upon cooling the sample slowly at an average rate of 3 °C/min.
SIS′₀.₃₃O-11. $T_{\text{ODT}}$S obtained from SAXS and rheological measurements are in much better agreement for this sample indicating an ODT at 180 °C. Upon heating to 120 °C from the freeze-dried state, reflections at $q/q^* = \sqrt{1}, \sqrt{3}, \text{and} \sqrt{4}$ can be seen, though the $\sqrt{3}$ peak is subtle (Figure 5.10a). Six-fold (Figure 5.11a) rotationally symmetric projections are evident in TEM images obtained from SIS′₀.₃₃O-11 annealed for 20 mins at 120 °C. Interestingly, large regions of 2-fold (possibly rhombohedral) rotational symmetry can also be observed (Figure 5.11b). Slight distortions from true six-fold symmetry observed in all images may be an artifact of the microtoming process but could also originate from a rhombohedral lattice. This point is discussed further in the next section. This phase is tentatively assigned the HEXₜ designation due to the presence of hexagonal symmetry, spherical domains, and phase behavior similarities to the sample studied by Zhang et al.¹⁴²,¹⁴³ Additionally, unusual patterns are observed at grain boundaries (Figure 5.11c).
Figure 5.10 (a) Synchrotron SAXS patterns collected during heating and cooling ramps for SIS′₀.₃₃O-11 reveal presence of the HEXs, σ, and BCC phases. Patterns observed during the heating ramp at 140 °C are consistent with (b) those observed by Zhang et al. in a symmetric SISO tetrablock ($M_n = 24.4$ kDa, $f_S = 0.56$, $f_I = 0.35$, $f_O = 0.09$) at 175 °C. (c) Annealing the sample for one day at 175 °C yielded TEM images possessing 12-fold rotational symmetry with quasicrystalline order. Adapted with permission from Zhang et al., *JACS*, 134, 7636-7639. Copyright 2012 American Chemical Society.

At intermediate temperatures between 140 and 150 °C, patterns lack sufficient detail to permit identification of the related morphology. However, analogous scattering patterns from a symmetric SISO sample ($M_n = 24.4$ kDa, $f_S = 0.56$, $f_I = 0.35$, $f_O = 0.09$) from Zhang et al. (Figure 5.10b) suggest the presence of a transitional quasicrystalline phase. Their reported scattering pattern at 175 °C is similar in intensity and peak positions to the one seen here upon heating to 140 °C (Figure 5.10a). However, while
5.3 Results

Figure 5.11 TEM images obtained from SIS$_{0.33}$O-11 annealed at 120 °C for 20 minutes reveals regions of (a) two-fold symmetry and (b) six-fold symmetry. (c) Unusual patterns are observed at grain boundaries. (d) Heating the same sample to 140 °C and annealing for an additional five minutes yields large regions of no apparent order.

Zhang et al. saw TEM images corresponding to the DDQC (Figure 5.10c), only a disordered (possibly liquid-like) packing of spheres is observed here (Figure 5.11d). This may draw from a disparity in annealing times; the sample here was first annealed at 120 °C for 20 minutes and then heated to 140 °C and annealed for an additional 5 minutes in order to mimic the heating ramp during SAXS experiments. In contrast, Zhang’s DDQC forming tetrablock had been annealed at 175 °C for one day. It is also possible that
quasicrystalline order exists in the current SIS'O sample but was simply not observed since it can only be seen in a small minority of projections.\textsuperscript{142} Heating the sample further causes a transition from $\sigma$ to disorder. Upon cooling, a pattern consistent with BCC is observed which leads to the $\sigma$ phase at intermediate temperatures and, finally, the HEX\textsubscript{s} phase at the lowest temperature of 100 °C. Quenching the sample from disorder to 155 °C also produced reflections consistent with the A15 phase (not shown), and additional peaks compatible with $P4_2/mnm$ symmetry. This result indicates a mixture of A15 and $\sigma$ upon quenching but was not reproducible. Still, observing additional ordered phases within these materials is feasible. It is worth noting that this sample is an exception to the trend of increasing $X_C$ and displays a broad melting transition indicative of a broader distribution of crystallite sizes in the sample.\textsuperscript{291}

**SIS'_{0.33}O-14 and SIS'_{0.33}O-15.** Both samples are identical in terms of phase behavior. Starting at 100 °C, heating both samples displays SAXS pattern consistent with the HEX\textsubscript{s} phase until disorder. Cooling from the disordered phase again reveals the same patterns. Representative SAXS patterns for SIS'_{0.33}O-15 during cooling and heating ramps are shown in Figure 5.12a. Supplemental TEM micrographs were generated this time by cooling from the disordered state followed by a 20 minute anneal at 220 °C (Figures 5.12b-c). Again, clear presence of six-fold rotational symmetry is revealed with a minority of distorted four-fold projections.
5.3 Results

Figure 5.12 (a) SAXS patterns during heating and cooling ramps for SIS\textsubscript{0.33}O-15 display reflections consistent only with the HEX\textsubscript{S} phase when ordered. SIS\textsubscript{0.33}O-14 displays the same scattering behavior. (b) Quenching from the disordered state at ~100 °C/min to multiple temperatures yields similar reflections. TEM images contain regions with (c) six-fold and (d) distorted four-fold rotational symmetry.
5.4 Discussion

The presence of core-shell domain geometries is now well established in sphere forming SISO tetrablock terpolymers. These nominally spherical domains have been shown to self-assemble in a variety of phases including LLP, DDQC, HEX\textsubscript{S}, BCC, A15, \(\sigma\), HCP, FCC, and a tentative rhombohedral phase.\textsuperscript{141–143,289} Previously, we identified the asymmetry parameter \(\tau\) as an important factor governing phase behavior.\textsuperscript{282,289} This identification was guided by intuition; as illustrated in Figure 5.13, the SIS' matrix has tremendous freedom since S blocks can loop back into the shell, bridge between neighboring micelles, or mix with the I block and form the matrix. The adjustable ratio of these three states endows the tetrablock with additional freedom in adjusting domain sizes. If S blocks favor looping configurations, the size of initial shell formed by the S' block is increased. Conversely, if S blocks favor bridging domains, the size of the bridge-connected domain can be increased. The ability of the SIS' matrix to intermix, especially at segregation strengths close to the ODT, enables access to a continuum of core-shell domain sizes between the aforementioned looping and bridging limits. This freedom likely plays a vital role in the formation of complex Frank-Kasper phases which can require up to five different sized Wigner Seitz cells.\textsuperscript{84,147}

It is unsurprising then that varying the \(\tau\) parameter, which characterizes molecular symmetry in the SIS' matrix, can have a serious impact on phase behavior. For example, while SIS'\textsubscript{0.33}O-14 (characterized in this report) displays only the HEX\textsubscript{S} phase for all temperatures, SIS'\textsubscript{0.68}O-14 (characterized previously\textsuperscript{289}) revealed the presence of nine different sphere-forming symmetries. Previous studies showed a tendency of tetrablocks to only display HEX\textsubscript{S} ordering at low \(\tau\) values.\textsuperscript{282,289} Zhang summarized the phase behavior of SIS'\textsubscript{0.21}O-16 and SIS'\textsubscript{0.32}O-07 (\(f_S/f_I \approx 1\)) in her dissertation and found exclusive presence of the HEX\textsubscript{S} phase at all temperatures.\textsuperscript{282} However, experiments reported here indicate that, while the HEX\textsubscript{S} phase is undoubtedly stabilized at low \(\tau\) values, a variety of morphologies can be observed in this region as \(f_O\) is varied including LLP, DDQC, \(\sigma\), and BCC.
5.4 Discussion

Figure 5.13 Illustration of the SIS′O core-shell structure showing the discrete states of microphase separation made available by the ABA′C molecular architecture. Terminal S (blue) blocks can loop back into S′ (blue) domains, bridge to neighboring S′ domains, or mix with the I (red) block.

Recent reports have enhanced our understanding of the relationships between these complex sphere-forming phases in both diblocks and tetrablocks and the data reported here reinforce these findings. For example, heating SIS′_0.33O-09 from a freeze-dried state leads to formation of the LLP phase which can transition to the DDQC phase upon heating or extended annealing at constant temperature. This result underscores the influence of temperature in the dynamics of phase formation in these materials. Heating further leads to a transition to the σ phase. Analogous results were obtained by Gillard et al. in low molecular weight poly(isoprene)-b-poly(lactide) (IL, \( M_n = 4.6 \text{ kDa}, f_L = 0.18 \)) diblocks that showed the LLP phase evolved when disordered spheres were rapidly quenched below a certain ergodicity temperature, \( T_{\text{erg}} \). This kinetically trapped, soft glass-like solid was necessary for development of the DDQC phase which evolved to the σ phase given enough time. These results expose the metastability of the DDQC and LLP phases and explain why they are not recovered when SIS′_0.33O-09 is cooled from the disordered state. We speculate that the freeze-dried state acts as an initial disordered state since quenching diblocks from the disordered phase yielded the same LLP as heating tetrablocks rapidly from the freeze-dried state.

Chapter 4 outlines how tetrablocks exhibit similar behavior but with additional caveats due to the possibility of segregation within the matrix. When SIS′O_0.73O-13 was rapidly heated to within 30 °C of the ODT, SAXS patterns consistent with LLP were observed. The sample transitioned to DDQC order with time and to σ upon increasing temperature, consistent with the results seen above. However, if the sample is cooled slowly, the σ
phase is not seen to be the stable morphology. The system transitions from $\sigma$ to metastable HCP and rhombohedral phases upon cooling. These order-order transitions are driven by domain rearrangement due to SIS' matrix segregation since mass exchange through chain diffusion is not facile at such high segregation strengths.\textsuperscript{289} Given these observations, the surprising stability of the HEX$_S$ phase in low $\tau$ tetrablocks is interesting. Even when SIS'$_{0.18}$O-16 or SIS'$_{0.33}$O-15 are slowly cooled (~3 °C/min) over 150 °C below $T_{ODT}$, the system does not transition away from the HEX$_S$ phase. Quenching SIS'$_{0.33}$O-15 (~100 °C/min) from the disordered state to various temperatures produced the same reflections (Figure 5.12b).

Another interesting result was the evolution of the DDQC from the HEX$_S$ phase shown by Zhang \textit{et al} in a symmetric SISO tetrablock ($M_n = 24.4$ kDa, $f_S = 0.56$, $f_I = 0.35$, $f_O = 0.09$).\textsuperscript{142} In SAXS studies, they observed a transition from the HEX$_S$ phase to the $\sigma$ phase through an intermediate (about 40 °C below $T_{ODT}$) which could not be conclusively identified based on scattering data alone (Figure 5.10b). Annealing this intermediate for an extended period yielded TEM images consistent with 12-fold quasicrystalline order (Figure 5.10c). A similar intermediate scattering pattern is observed here for SIS'$_{0.33}$O-11 (Figure 5.10a) between the HEX$_S$ and $\sigma$ phases. TEM images of SIS'$_{0.33}$O-11 annealed only for 20 minutes at 120 °C reveal exquisite ordering in these materials displaying 4-fold and 6-fold rotational symmetry (Figure 5.11a-c). It is interesting to note that if the same sample is heated further to 140 °C (again, about 40 °C below $T_{ODT}$) and annealed for an additional five minutes, no large regions of ordering are observed. Instead the TEM images display a disordered packing of micelles (Figure 5.11d) suggesting an initial diffusion-less rearrangement of the spherical domains as they attempt to transition to the $\sigma$ phase. This observation is consistent with the high segregation present in the material ($T_{ODT} = 185$ °C) which hampers chain exchange and prevents facile rearrangement. Perhaps long term annealing of this sample would lead to patterns consistent with quasicrystalline order as the sample attempts to transition from this seemingly disordered arrangement of spheres (akin to LLP) to the $\sigma$ phase. This
5.4 Discussion

reasoning is consistent with the results of Zhang et al. who observed the DDQC in SISO tetrablocks only when the sample was annealed for one day at 40 °C below the ODT.\(^\text{142}\)

Despite its near ubiquitous appearance in low \(\tau\) tetrablocks, the structure of the HEX\(_S\) phase is still not completely understood. It was postulated that HEX\(_S\) possesses simple hexagonal symmetry (space group \(P6/mmm\) as shown in Figure 5.2) leading to 6-fold and 4-fold rotationally symmetric projections. Although the curious scattering patterns account for the 6-fold in-plane symmetry, they do not produce any additional reflections due to scattering from the \((hkl, l \neq 0)\) planes. The authors reasoned this may be due to disorder along the c-axis which extinguishes reflections that would have resulted from correlations between the 6-fold rotationally symmetric planes.\(^\text{143}\) Given the additional TEM and scattering data on low-\(\tau\) tetrablocks, we speculate additional details that refine the structure proposed previously. The TEM data clearly illustrates the HEX\(_S\) phase is composed of spherical O cores and this conclusion can be reinforced using a simple calculation. For example, SIS'\(_{18}\)O-16 contains \(f_O = 0.16\) and (assuming a HEX\(_C\) morphology) SAXS data indicates \(d_{10} = 18.3\) nm. These values can be used to extract a hard cylinder radius for the O domain of \(r_{cyl} = 3.9\) nm. TEM images obtained from this sample yield an average radius of domains to be \(5.8 \pm 0.7\) nm, supporting the presence of significantly larger cores which must be spherical. However, it is important to note that TEM data cannot be used to comment on the structure of the surrounding intermixed SIS' matrix. The nature of this matrix undoubtedly plays a role in stabilizing the HEX\(_S\) phase and, in analogy to the cylinder-to-sphere transition in diblocks, we propose here a new structure for this morphology which is consistent with both SAXS and TEM results.

Koppi et al. characterized the cylinder-to-sphere order-order transition in poly(ethylene-propylene)-\(b\)-poly(ethylethylene) (PEP-PEE) diblock melts using a combination of rheology and small-angle neutron scattering (SANS).\(^\text{292}\) They studied the epitaxial growth of the BCC phase as temperature is increased starting from a shear-aligned HEX\(_C\) morphology and established that the transition from a cylindrical to spherical microstructure proceeds through an undulating HEX\(_C\) intermediate as shown in Figure 5.14a. Their structural diagram is used as the basis for the HEX\(_S\) structure.
proposed here (Figure 5.14b). We hypothesize that the HEXS structure possesses a domain morphology which is a hybrid of core-shell micelles and core-shell cylinders. Such domains are characterized by spherical O cores contained within undulating SIS’ cylinders but, due to the staining method, produce TEM images which only indicate the presence of micellar domains. The cylinders orient on a hexagonal lattice with O cores possessing no axial periodicity. Note that this changes the symmetry of ordering from space group \( \text{P6/mmm} \) to plane group \( \text{p6mm} \) (or more concisely, \( \text{p6m} \)) and is consistent with the observed scattering patterns. Figure 5.11d displays TEM results which capture the distorted four-fold symmetry indicating short-range axial order. Images with longer range six-fold symmetry are much more prevalent (Figures 5.8a, 5.10b, 5.10c, and 5.11a). Importantly, the formation of cylinder-like matrix domains with embedded spherical cores is not accessible to a diblock architecture and, accordingly, spheres oriented on a simple hexagonal lattice have not been reported for the AB architecture.

Such a structure can also be used to rationalize the stability of the HEXS structure with regards to \( \tau \), O content, and temperature. At \( \tau = 0.33 \), complex sphere forming phases are prevalent from \( 0.09 \leq f_0 \leq 0.11 \). However, in samples with a higher O content, SIS’\(_{33}\)O-
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14 and -15, HEX$_S$ is observed at all temperatures below $T_{ODT}$. This is curiously analogous to diblock phase behavior where decreasing compositional asymmetry between the matrix and discontinuous blocks stabilizes cylindrical domains over spherical ones. The unique molecular architecture of the tetrablock terpolymer and especially the presence of an S’ shell may prohibit the facile fusion of O cores required to form the HEX$_C$ phase leading to stabilization of the proposed HEX$_S$ structure.\textsuperscript{292} In SIS’$_{33}$O-11, the HEX$_S$ phase is seen at $T = 120 \, ^\circ C$ before increasing temperature drives a transition to spherical morphologies analogous to the cylinder-to-sphere OOTs observed in diblocks upon heating. The striking grain boundaries observed through TEM characterization in this sample (Figure 5.10c) show regions where the HEX$_S$ domains are disrupted and spherical micelles can form. It is interesting to note that the angles between these grains are approximately $30^\circ$; the intersection of these six-fold rotationally symmetric grains at such an angle may form the underlying hexagonal antiprisms which are prevalent in the $\sigma$ phase observed at higher temperatures. At $\tau = 0.18$, only the HEX$_S$ phase is observed at all temperatures in both SIS’$_{18}$O-11 and -15. Clearly, these stark phase behavior differences between SIS’$_{33}$O-11 and SIS’$_{18}$O-11 arise from adjusting the $\tau$ parameter which seems to favor cylinder-like matrix domains at lower values. As the symmetry parameter is increased, the region for observing sphere-forming morphologies widens. Both the data reported here and the theoretical and experimental results shown in Chapter 4 reinforce this claim. Clearly, more quantitative SCFT calculations are required to support this hypothesis by elucidating block placement within the HEX$_S$ phase as $f_O$ and $\tau$ are varied.

The experiments reported here establish that the HEX$_S$ phase can be obtained reversibly from the disordered phase and that low $\tau$ samples also exhibit a richness in sphere forming phase behavior. The proposed HEX$_S$ structure is capable of rationalizing both TEM and scattering results, and captures phase behavior trends as temperature, $f_O$, and the $\tau$ parameter are adjusted. Despite these advancements, it may be worth exploring other material classes for clues that can further elucidate the HEX$_S$ morphology. Frank-Kasper phases of space group $P6/mmm$ and $P6/mmm$ have been postulated\textsuperscript{146,293,294} and
many alloy structures possessing this symmetry exist. Exploring such seemingly disparate material classes may yield additional insights into the formation of the HEXs phase. Field theory calculations, which have advanced significantly and are already being used to elucidate ABAC tetrablock phase behavior, will be of significant utility in understanding tetrablock self-assembly and exploring new candidate structures.

5.5 Conclusions

A series of SIS′O tetrablock terpolymers of low molecular asymmetry (τ ≤ 0.33) spanning 0.4 ≤ fO ≤ 0.16 were synthesized and characterized through a combination of SAXS, TEM, DMS, and DSC. Experiments yielded evidence for the existence of a variety of sphere-forming phases including LLP, DDQC, σ, BCC, and HEXs. The HEXs morphology was found to be stable over a large region of phase space in multiple samples and could be attained reversibly from the disordered state. On the basis of scattering and TEM data, we hypothesize the HEXs structure is composed of hexagonally packed undulating cylinders that are decorated with spherical O cores. These cores are arranged aperiodically along the cylinder axis leading to the p6mm scattering observed within the HEXs phase.

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Chapter 6

Phase Behavior of Symmetric Poly(isoprene)-\textit{b-}poly(styrene)-\textit{b-}poly(isoprene)-\textit{b-}poly(ethylene oxide) Tetrablock Terpolymers

6.1 Introduction

The simplest of block copolymers, an AB diblock, is well-known to produce at least four stable phases depending on the volume fraction of the constituent blocks: spheres packed on a body-centered cubic lattice (BCC), hexagonally packed cylinders (HEXC), gyroid, and lamellae. Even after decades of experimental and theoretical efforts, this apparently simple molecule continues to produce new, fascinating self-assembled structures including the complicated Frank-Kasper σ phase and a dodecagonal quasicrystal. The phase behavior of diblocks can primarily be captured through two variables: the product $\chi_{AB}N$, termed the segregation strength, and $f_A$, the volume fraction of block A. Adding a third chemically distinct block results in an ABC triblock terpolymer and vastly expanded parameter space ($f_A, f_B, \chi_{AB}, \chi_{BC}, \chi_{AC},$ and $N$). Consequently, changing both the chemistry (replacing A, B, or C) and block connectivity (ABC vs. BAC) can significantly impact the resulting morphology. Exploring this large phase space required the experimental efforts of several groups in order to elucidate the
rich phase behavior of these triblock terpolymers.\textsuperscript{112–129} Input from self-consistent field theory (SCFT) calculations frequently addressed ambiguities and aided in the identification of these morphologies.\textsuperscript{106,107,110,111}

In order to establish universality and capture the phase behavior of all possible ABC systems, Bailey et al. proposed a categorization system based on the relevant values of the Flory segment-pair interactions, $\chi_{AB}$, $\chi_{BC}$, and $\chi_{AC}$.\textsuperscript{130} Here, triblocks where A/C interfaces are enthalpically preferred over required but unfavorable B/C and A/B interfaces were called “frustrated”. This category can be further divided into type I frustration ($\chi_{BC} \geq \chi_{AC} \geq \chi_{AB}$) and type II frustration ($\chi_{BC} \geq \chi_{AB} \geq \chi_{AC}$). Triblocks in which A/B and B/C interfaces are least enthalpically costly do not favor the formation of A/C interfaces and were termed “non-frustrated”. Using this classification scheme, Bailey et al. systematically studied the phase behavior of ABC triblock terpolymers containing poly(styrene) (S), poly(isoprene) (I), and poly(ethylene oxide) (O) where $\chi_{SI} \approx \chi_{SO} << \chi_{IO}$. Non-frustrated poly(isoprene)-b-poly(styrene)-b-poly(ethylene oxide) (ISO) and frustrated poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide) (SIO) triblocks of similar molecular weights and volume fractions were examined in order to elucidate phase behavior differences resulting only from the frustration condition.

Each SIO or ISO sample used in this study was synthesized using a common parent diblock assuring that each triblock lies on the constant $f_S = f_I$ isopleth. As expected, the morphological behavior of I, S, and O containing triblock terpolymers was significantly influenced by block sequence. Both ISO and SIO tetrablocks formed two- and three-domain lamellae at $f_O \approx 0$ and $f_O \approx 0.25$, respectively. However, the phases observed between these two limits were very different. Four morphologies were observed between the lamellar phases in SIO: a pillared lamellar structure (PLS), hexagonally packed core-shell cylinders (CSC), penta-continuous core-shell gyroid (CSG), and semi-perforated lamellae (SPL). Both PLS and SPL morphologies formed A/C interfaces which illustrated the importance of frustration in determining phase behavior.\textsuperscript{131} In contrast, only one morphology was reported between the limiting lamellar cases in ISO: a non-cubic, triply periodic network phase called O$^{70}$ (space group $Fddd$).\textsuperscript{132} The same structure was
identified in poly(cyclohexylethylene)-b-poly(ethylethylene)-b-poly(ethylene) (CEE)\textsuperscript{133} and poly(ethylene)-b-poly(cyclohexylethylene)-b-poly(dimethyldisiloxane) (CED)\textsuperscript{134} samples, indicating a degree of universality to this morphology. Current interest in exploring network phases led to further synthetic and characterization efforts focused on examining the ISO system along other $f_S/f_I$ isopleths leading to identification of the BCC morphology and two additional network phases, Q\textsuperscript{230} and Q\textsuperscript{214}.\textsuperscript{135–138}

In order to expand the range of compositions and chemistries which lead to network phase formation, ABAC type tetrablock terpolymers were studied next. It was expected that the asymmetric placement of two separate A blocks would present different phase behavior. Indeed, varying the previously studied CED triblock terpolymers to a CECD-type architecture produced O\textsuperscript{52}, another network phase.\textsuperscript{302} Though this phase had been observed previously in CEE triblocks, it formed only after a shear-induced phase transition.\textsuperscript{133} Similar studies were conducted by varying the S block placement in the non-frustrated ISO triblock to produce a SISO tetrablock terpolymers.\textsuperscript{141} During initial studies, volume fractions of each block and overall molecular weight were matched between the ISO and SISO polymers in order to study phase behavior differences arising from molecular architecture alone. However, in stark contrast to the triblock case, no network phases were observed during initial studies of SISO polymers; only liquid-like packing of spheres and hexagonally packed cylinders were found.\textsuperscript{141} Instead, further experiments discovered a rich assortment of nominally sphere-forming ordered phases including the Frank-Kasper σ phase, Frank-Kasper A\textsubscript{15} phase, dodecagonal quasicrystal, simple hexagonal packing (HEX\textsubscript{s}), hexagonal close packing (HCP), face-centered cubic (FCC), BCC, and a tentatively assigned rhombohedral phase.\textsuperscript{141–143,289} Interestingly, some of the same complex phases seen in tetrablocks were also observed in diblocks around the same time indicating some degree of universality in the formation of these materials.\textsuperscript{92,93} In fact, the same complex phases have been observed across seemingly disparate material classes such as intermetallic alloys,\textsuperscript{148,283} surfactants,\textsuperscript{90,261,262} lipids,\textsuperscript{263–266} hybrid nanoparticles,\textsuperscript{267–269} and dendrimers.\textsuperscript{86,270–272} The exploration of these parallels has yielded a deeper understanding of differences and similarities in self-assembly between
hard and soft materials. Combined, these recent findings have motivated a renewed interest in the phase behavior of sphere forming block polymers.

The studies listed above clearly illustrate the influence of frustration (SIO vs. ISO) and molecular architecture (SIO vs. SISO) in the phase behavior of block terpolymers. The focus of this chapter is to extend the above studies by probing the phase behavior of poly(isoprene)-b-poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide) (ISIO, Figure 6.1), the tetrablock analog of the frustrated ISO triblock system. Two series of ISIO tetrablocks are synthesized using anionic polymerization and characterized through a combination of DMS, SAXS, and TEM. Simulation tools made available by the open-source Polymer Self-Consistent Field (PSCF) code are exploited to study equilibrium phase behavior and domain geometry. The ordered morphologies observed include BCC packed spheres and hexagonally packed cylinders.

![Figure 6.1](image_url) Molecular structure of poly(isoprene)-b-poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide) tetrablock terpolymer. Note that about seven percent of the isoprene repeat units have a 3,4 microstructure.

6.2 Methods

6.2.1 Polymer Synthesis

The poly(isoprene)-b-poly(styrene)-b-poly(isoprene)-b-poly(ethylene oxide) (ISIO) tetrablock terpolymers used in this study were prepared using a two-step anionic polymerization procedure. Details of the monomer and solvent purification and polymerization procedure are described elsewhere. In the first step, isoprene polymerization was initiated by sec-butyllithium at 40 °C in cyclohexane under an argon atmosphere. Subsequently, carefully metered amounts of styrene and isoprene were sequentially introduced to the reactor. Aliquots were taken before each monomer charge...
for SEC and \(^1\)H NMR. After completion of the ISI polymerization, a 10-fold molar excess of ethylene oxide, relative to sec-butyllithium, was added to the solution and allowed to react for 2 h resulting in the addition of a single \(-\text{CH}_2\text{CH}_2\text{O}-\) unit to each polymer chain.\(^{304}\) The reaction was terminated with excess degassed methanol, yielding a hydroxyl end-capped poly(isoprene)-\(b\)-poly(styrene)-\(b\)-poly(isoprene) triblock (ISI-OH). ISI-OH was precipitated in methanol, decanted, filtered, and freeze-dried from benzene. In the second step, ISI-OH was reinitiated by reaction with potassium naphthalenide in tetrahydrofuran at 40 °C followed by the introduction of a carefully measured amount of ethylene oxide. The monomer was allowed to react for 24 h prior to termination with excess degassed methanol. This method allows the facile synthesis of multiple tetrablocks containing different lengths of O from a single batch of ISI-OH precursor; the synthetic route is illustrated in Figure 6.2. Excess THF was removed by rotary evaporation and the resulting polymer was re-dissolved in chloroform. The solution was washed once with a saturated sodium bicarbonate solution followed by multiple water washes to remove residual acid and salts. The polymer was recovered by rotary evaporation of the remaining chloroform. Then, 0.5 wt % (relative to tetrablock mass) butylated
hydroxytoluene was added to prevent oxidation and the polymer was freeze-dried from benzene.

### 6.2.2 Molecular characterization

Size-exclusion chromatography (SEC) analysis was performed on three Phenogel (Phenomenex) columns (1000, 5000 and 500 Å pore size) with THF eluent at 25 °C with a flow rate of 1.0 mL/min controlled by a Waters 590 Programmable HPLC pump using a Waters 717 Autosampler and a Waters 410 Refractometer. All SEC data reported here have been normalized using the maximum peak intensity of each trace. The number average molecular weight of the first I block \( (M_{n,I}) \) and the molecular weight distributions and dispersity indices for IS, ISI, and ISIO were obtained using SEC, operated with THF as the mobile phases and calibrated with polystyrene standards (Polymer Laboratories). The following Mark-Houwink parameters were used to obtain the molecular weight of the I block: \( K = 15.7 \) (dL/g \( \times 10^5 \)), \( a = 0.736 \).\(^{305}\) The overall number-average molecular weight \( (M_{n,ISIO}) \) was calculated using \( M_{n,I} \) and the weight fractions determined using \(^1\)H NMR. NMR spectra were acquired with CDCl\(_3\) as the solvent on a Varian VI-500 spectrometer and referenced to the residual solvent peak. The mole fractions of poly(styrene), poly(isoprene), and poly(ethylene oxide) blocks were quantified using the integrated areas under well-defined resonances, and these values were subsequently converted to weight fractions. Volume fractions were obtained by using published homopolymer densities at 140 °C \( (\rho_S = 0.969 \text{ g/cm}^3, \rho_I = 0.830 \text{ g/cm}^3, \rho_O = 1.064 \text{ g/cm}^3) \).\(^{167}\) All samples discussed here are referred to as \( \text{ISI}_X\text{O}-f_O \) where \( X \) represents the molecular weight of the ISI precursor in kDa and \( f_O \) is the volume fraction of O within the tetrablock sample. Representative SEC and \(^1\)H NMR traces are shown in Figures 6.3 and 6.4, respectively.

### 6.2.3 Small angle X-ray scattering

Synchrotron SAXS experiments were conducted at 12-ID-B beamline at the Advanced Photon Source (Argonne National Laboratory, Argonne, IL, USA) using \( \lambda = 0.886 \) Å wavelength X-rays and a sample-to-detector distance of approximately 4 m. 2D data were collected on a Pilatus 2M semiconductor hybrid pixel detector and azimuthally averaged.
6.2 Methods

Figure 6.3 Representative SEC traces obtained from final ISIO tetrablock and intermediate aliquots.

Figure 6.4 Representative $^1$H NMR spectrum for final ISIO tetrablocks. Protons corresponding to each relevant peak are labeled.
SAXS results are reported as intensity vs scattering wave vector magnitude $q = |\vec{q}| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$, where $\theta$ is the scattering angle. Specimens (10-20 mg) were hermetically sealed in aluminum DSC pans. Data were obtained by rapidly heating (~130 °C/min) freeze-dried or annealed samples (as indicated in results section) to the target temperature before collecting patterns. Temperature was controlled within ±1 °C using a Linkam DSC stage.

6.2.4 Transmission electron microscopy

TEM data were obtained on a Tecnai G2 Spirit BioTWIN transmission electron microscope operating at 120 keV at the University of Minnesota Characterization Facility. Samples were annealed under vacuum at specified temperatures and then quenched in liquid nitrogen to preserve the melt-state morphology. Thin slices (~50 nm) were obtained using a Leica UC6 ultramicrotome fitted with a Diatome diamond knife. Sections were collected on copper grids (Ted Pella) and stained using the vapor from a 2% aqueous OsO$_4$ solution for 15 min to obtain electron contrast; this reagent reacts preferentially with poly(isoprene) and renders I domains dark in the TEM images.

6.2.5 Dynamic mechanical spectroscopy

Linear DMS data were obtained using a Rheometric Scientific ARES strain-controlled rheometer fitted with 25 mm diameter parallel plates. All experiments were performed significantly above the glass transition and melting temperatures of the PS and PEO blocks, respectively, as determined by DSC measurements. Samples were prepared by compression molding the polymer powder into a 0.8 mm thick by 25 mm diameter disk at 150 °C under 2000 psi pressure for 5 min. The disk was heated to 10 °C above $T_{ODT}$ or 240 °C to minimize the effects of prior thermal history. Isochronal (1 rad/s) temperature ramp tests were performed at a strain amplitude of 1% at 2 °C/min to inform SAXS studies. Isothermal frequency sweep data were collected at select temperatures. Strain amplitude was set below the onset of nonlinearity as determined by strain sweeps between 0.1 and 10% at representative measurement temperatures.
6.2 Methods

6.2.6 Differential scanning calorimetry

DSC experiments were conducted on a TA instruments Q1000 DSC. 5-10 mg of polymer was heated to 150 °C (well above the \( T_g \) of S) to minimize the effects of prior thermal history. The sample was then cooled to -100 °C at 10 °C/min and data were collected during the second heating cycle, also at 10 °C/min. The degree of crystallinity of the PEO block was determined by normalizing the integrated melting peak to the bulk heat of fusion of PEO (213 J/g) as 

\[
\chi_c = \frac{\Delta H_m}{w_{PEO} \Delta H_{PEO, bulk}}
\]

6.2.7 Theoretical calculations

Self-consistent field theory (SCFT) is among the most powerful tools to study the phase behavior of block polymers.\(^{30,32}\) The success of SCFT has been demonstrated previously in discovering new ordered structures\(^{36,275}\) as well as aiding in understanding the complex morphologies observed experimentally in block copolymers.\(^{37,276}\) SCFT is a mean-field theory that is strictly valid in the limit of infinitely long chains; as a result, it captures the order-disorder transitions only qualitatively, but predicts the relative stability of competing ordered phases with reasonable accuracy.

Although SCFT has been discussed previously,\(^ {32,275,277,278}\) a brief overview is provided here to emphasize its important features. The SCFT framework is typically based on the standard Gaussian model, in which the polymer chains are treated as infinitely thin threads and their configurations are modeled using random-walk statistics.\(^ {34}\) The local interactions driving de-mixing of dissimilar segments are modeled using are Flory-Huggins interaction parameters \( \chi_{JK} \), while short-ranged hard-core repulsions are enforced by an incompressibility constraint.\(^ {34}\) Within this description, the SCFT formalism results in a set of coupled non-linear equations that are solved numerically.\(^ {277,278}\) Each self-consistent solution obtained in this way corresponds to a stable or metastable state which can be associated with a mesophase; a spatially periodic solution represents an ordered structure while a homogenous solution corresponds to the disordered phase. From such a solution, one can calculate relevant structural and thermodynamic quantities, such as free energy, domain spacing, and density profiles of different monomer types in the
mesophase. In order to construct the phase diagram, the thermodynamically stable phase is determined by comparing the free energy of all competing mesophases. The inherent challenge in constructing the phase diagram is the need to know all the possible phases \textit{a priori}, resulting in the assumption that all the competing phases are already known.

The SCFT parameter space for the ISIO tetrablock terpolymers involves five parameters: $\chi_{IS}$, $\chi_{SO}$, $\chi_{IO}$, $f_0$ and $f_i$, assuming the statistical segment lengths of all the monomer types are known. The degree of polymerization, $N$, is determined using the volume fractions and molecular weights of the different monomer types reported in experiments. Temperature independent statistical segment lengths are $b_I = 0.60$ nm, $b_S = 0.54$ nm and $b_O = 0.78$ nm, for the PI, PS and PEO respectively, calculated for the common reference volume $v_{\text{ref}} = 0.118$ nm$^3$. The following effective binary interaction parameters were used ($T$ is in units of Kelvin):

$$\chi_{IS} = \frac{26.4}{T} - 0.0288,$$

$$\chi_{IO} = \frac{108.8}{T} - 0.0695,$$

$$\chi_{SO} = \frac{59.6}{T} - 0.0458.$$

These interaction parameters were obtained by adjusting the parameters published by Frienlinghaus et al.\textsuperscript{279} in order to best match the experimental order-disorder and order-order transitions reported by Bluemle et al.\textsuperscript{141} at 140 °C with mean-field theoretical predictions. It should be emphasized here that the choice of interaction parameters certainly affects the relative stability of different phases. Due to the chemical similarity, these $\chi$ parameters should provide a reasonable qualitative understanding for the ISIO system.
6.3 Results

The phase behavior of SISO tetrablocks with a symmetric SIS precursor has been well studied. In order to highlight the influence of frustration on phase behavior given an ABAC-type molecular architecture, nine symmetric ISI\textsubscript{19}O samples were synthesized with similar molecular weights and volume fractions as the previously studied SISO tetrablock. Additional ISI\textsubscript{30}O tetrablocks of a higher molecular weight were also synthesized for further studies as discussed in the following section. Molecular and thermal characterization data for these polymers have been summarized in Table 6.1. The following sections outline the results of morphological characterization of these samples through a combination of DSC, SAXS, TEM and DMS.

6.3.1 ISI\textsubscript{19} and corresponding ISI\textsubscript{19}O tetrablocks

Figure 6.5 shows the DSC curves for ISI\textsubscript{19}O tetrablock terpolymers. The ISI\textsubscript{19} endotherm indicates $T_{g,I} = -56$ °C and $T_{g,S} = 49$ °C; the latter is obscured by the melting peak of the O domains in samples with $f_O \geq 0.07$. These O melting peaks and the corresponding melting temperature increase with increasing $f_O$. The percent crystallinity of the O domains is summarized in Table 6.1. It should be noted that the melting temperature of the O domain, $T_{m,O}$, remains slightly below the melting temperature of a PEO homopolymer.
Table 6.1 Molecular and thermal characterization data for ISI_{19}, ISI_{30}, and respective tetrablocks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$f_S^a$</th>
<th>$f_I^a$</th>
<th>$f_O^a$</th>
<th>$M_n$ (kDa)$^b$</th>
<th>$D$</th>
<th>$T_{ODT}$ (°C)$^c$</th>
<th>$X_c^d$</th>
<th>$T_{m,O}$ (°C)$^d$</th>
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<tr>
<td>ISI_{19}</td>
<td>0.51</td>
<td>0.49</td>
<td>-</td>
<td>18.9</td>
<td>1.03</td>
<td>&lt;80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ISI_{19}O-03</td>
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<td>0.48</td>
<td>0.03</td>
<td>19.6</td>
<td>1.04</td>
<td>&lt;80</td>
<td>0</td>
<td>41</td>
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<tr>
<td>ISI_{19}O-07</td>
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<td>0.46</td>
<td>0.07</td>
<td>20.6</td>
<td>1.04</td>
<td>90</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>ISI_{19}O-10</td>
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<td>0.44</td>
<td>0.10</td>
<td>21.2</td>
<td>1.04</td>
<td>108</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>ISI_{19}O-15</td>
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<td>0.42</td>
<td>0.15</td>
<td>22.7</td>
<td>1.04</td>
<td>188</td>
<td>47</td>
<td>49</td>
</tr>
<tr>
<td>ISI_{19}O-20</td>
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<td>0.39</td>
<td>0.20</td>
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<td>1.04</td>
<td>&gt;240</td>
<td>53</td>
<td>54</td>
</tr>
<tr>
<td>ISI_{19}O-22</td>
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<td>0.38</td>
<td>0.22</td>
<td>25.2</td>
<td>1.04</td>
<td>&gt;240</td>
<td>53</td>
<td>55</td>
</tr>
<tr>
<td>ISI_{19}O-24</td>
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<td>0.37</td>
<td>0.24</td>
<td>25.8</td>
<td>1.04</td>
<td>&gt;240</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>ISI_{19}O-28</td>
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<td>0.35</td>
<td>0.28</td>
<td>28.7</td>
<td>1.04</td>
<td>&gt;240</td>
<td>51</td>
<td>57</td>
</tr>
<tr>
<td>ISI_{19}O-32</td>
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<td>0.33</td>
<td>0.32</td>
<td>29.2</td>
<td>1.04</td>
<td>&gt;240</td>
<td>52</td>
<td>59</td>
</tr>
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<td>ISI_{30}</td>
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<td>0.49</td>
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<td>29.6</td>
<td>1.03</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ISI_{30}O-02</td>
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<td>0.02</td>
<td>30.4</td>
<td>1.03</td>
<td>&lt;100</td>
<td>0</td>
<td>-</td>
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<td>0.47</td>
<td>0.04</td>
<td>31.1</td>
<td>1.03</td>
<td>&lt;100</td>
<td>47</td>
<td>39.2</td>
</tr>
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<td>0.06</td>
<td>32.0</td>
<td>1.03</td>
<td>105</td>
<td>49</td>
<td>41.7</td>
</tr>
<tr>
<td>ISI_{30}O-10</td>
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<td>0.44</td>
<td>0.10</td>
<td>33.5</td>
<td>1.03</td>
<td>182</td>
<td>56</td>
<td>46.0</td>
</tr>
<tr>
<td>ISI_{30}O-21</td>
<td>0.40</td>
<td>0.39</td>
<td>0.21</td>
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<td>1.03</td>
<td>&gt;240</td>
<td>67</td>
<td>55.3</td>
</tr>
</tbody>
</table>

$^a$Volume fractions obtained from $^1$H NMR. $^b$M$_n$ obtained through a combination of SEC and $^1$H NMR. $^c$T$_{ODT}$ estimated from rheological temperature ramps. $^d$Obtained using DSC.
6.3 Results

Figure 6.5 DSC endotherms near the melting point of the O domain for ISI$\text{I}_{19}$ (inset) and corresponding ISI$\text{I}_{19}$O tetrablocks. Curves have been shifted vertically for clarity.

**ISI$\text{I}_{19}$ and ISI$\text{I}_{19}$O-03.** Both ISI$\text{I}_{19}$ and ISI$\text{I}_{19}$O-03 remain disordered over the relevant temperature range ($T > 80 \, ^\circ\text{C}$). Representative SAXS and DMS are shown in Figure 6.6. The frequency sweep plots were constructed using time-temperature superposition (TTS) with a reference temperature ($T_{\text{ref}}$) of $80 \, ^\circ\text{C}$. It should be noted that TTS is not fundamentally valid for rheologically complex materials such as block copolymers. Here, this technique is used only to allow facile comparison of data obtained over a wide range of temperatures. The single broad peak seen within scattering data from both ISI$\text{I}_{19}$ and ISI$\text{I}_{19}$O-03 (Figure 6.6a) indicate a disordered state. ISI$\text{I}_{19}$O-03 (Figure 6.6b) displays nearly terminal behavior ($G' \sim \omega^2$, $G'' \sim \omega$) corroborating this conclusion.

**ISI$\text{I}_{19}$O-07 and ISI$\text{I}_{19}$O-10.** Scattering data for these tetrablocks (Figure 6.7a) show the appearance of a second peak at a lower $q$ than the broad peak seen in lower $f_\text{O}$ samples.
6.3 Results

Figure 6.6 (a) Scattering data at 80 °C for ISI19 and ISI19O-03 and (b) frequency sweep data for ISI19O-03. All data indicate that these samples remain disordered over the relevant temperature range ($T > T_{g,s}$). Frequency sweep data display nearly terminal scaling.

Figure 6.7 (a) Scattering data at 80 °C for ISI19O-07 and ISI19O-10. Data indicates the emergence of segregated O domains. (b) Frequency sweep data for ISI19O-10.
6.3 Results

Figure 6.8 (a) Synchrotron SAXS patterns for ISI$_{19}$O-15 display reflections consistent with the BCC phase at all temperatures before disorder. (b) Frequency sweep data are consistent with the presence of a cubic morphology.

The peaks sharpen as O content is increased indicating stronger segregation between domains. Representative frequency sweep data taken from ISI$_{19}$O-10 (Figure 6.7b) displays terminal scaling at lower frequencies. However, the region between $\omega = 10^0$ to $10^1$ rad/s contains data that does not superimpose which may derive from the non-equilibrium state of the sample. It was hypothesized that close proximity between the glass transition of the S domain ($T_{g,S} \approx 80$ °C) and the ODT ($T_{ODT} = 108$ °C) does not allow the sample to develop long-range order. Higher molecular weight analogs were made to further separate $T_{g,S}$ and $T_{ODT}$ and allow additional studies of the phase behavior in this range of $f_O$ (results are presented in section 6.3.2).

**ISI$_{19}$O-15.** Synchrotron SAXS patterns produced by this sample display peaks at $q/q^* = \sqrt{1}, \sqrt{2}, \sqrt{3}, \sqrt{5}, \sqrt{6}, \sqrt{7}$, indicating a BCC morphology (Figure 6.8a). Frequency sweep data indicate a low frequency plateau in $G'$ observed in ISI$_{19}$O-15 (Figure 6.8b) consistent with a cubic phase with three dimensional translation order.
6.3 Results

Figure 6.9 (a) SAXS patterns collected for ISI$_{19}$O-20 reveal hexagonal symmetry at and below 160 °C while reflections consistent with BCC symmetry are seen above the OOT. (b) Temperature ramp data collected during a heating cycle after disordering also display the OOT. Increase in the moduli is consistent with the transition from a 2D hexagonal to cubic morphology. (c) TEM images help confirm that the phase below 160 °C is composed of cylindrical, not spherical, domains.

**ISI$_{19}$O-20.** SAXS patterns are shown in Figure 6.9a from a temperature range of 80 °C to 240 °C. Though the sample does not disorder in this temperature range, it is not heated above 240 °C to avoid the effects of thermal degradation. Below 160 °C, the SAXS patterns (Figure 6.9a) display reflections at $q/q^* = \sqrt{1}, \sqrt{3}, \sqrt{4}, \sqrt{7}$, and $\sqrt{9}$ which are consistent with hexagonal ordering. Patterns collected above 180 °C display reflections at $q/q^* = \sqrt{1}, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}, \sqrt{6}, \sqrt{7}$. Due to the mass exchange taking place within the sample around the order-order transition (OOT), the reflections at 180 °C qualitatively
look consistent with BCC but quantitatively show slight deviations from expected $q$ positions. A rheological signature of the OOT is also apparent in the temperature sweep data (Figure 6.9b). Around 162 °C, the data displays a rapid upturn till approximately 179 °C; the rapid increase in modulus is consistent with the transition from a 2D hexagonal packed cylinders to a 3D cubic structure.\textsuperscript{169} However, it is still important to confirm the domain geometry within the hexagonal structure due to the recent discovery of a simple hexagonal phase in ABAC-type tetrablock terpolymers which display scattering consistent with HEXc but contain spherical domains.\textsuperscript{143} To this end, TEM micrographs help verify that the domain morphology is indeed cylindrical at temperatures below $T_{OOT}$ (Figure 6.9c). Analysis of the FFT (inset) reveals that $d_{10,TEM}$ equals 23.3±1.9 nm which is consistent with the $d_{10}$ of 22.0 nm obtained from SAXS studies.

**ISI\textsubscript{19O-22, ISI\textsubscript{19O-24, ISI\textsubscript{19O-28, and ISI\textsubscript{19O-32.** Scattering data for these four samples at 140 °C is shown in Figure 6.10a. These samples do not display a $T_{OOT}$ or $T_{ODT}$ within the experimental temperature range of 80 °C $\leq T \leq$ 240 °C. Patterns display peaks at $q/q^* = \sqrt{1}, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}$ consistent with a hexagonal symmetry. Samples with a high $f_O$, and consequently higher molecular weight, display relatively poor ordering indicated by the broader Bragg peaks. Representative frequency sweep data is shown in Figure 6.10b. The decreasing response of $G'$ and $G''$ with decreasing frequency is associated with the 2D hexagonal cylinder phase.

**6.3.2 ISI\textsubscript{30 and corresponding ISI\textsubscript{30O tetrablocks**

The ISI\textsubscript{30O series of tetrablock terpolymers were synthesized to further probe the phase behavior of samples with 0.07 $\leq f_O \leq$ 0.10. ISI\textsubscript{19O-07 and ISI\textsubscript{19O-10 only displayed two broad peaks before disordering but a slightly larger molecular weight may promote long-range ordering before the sample melts. Figure 6.11 displays the DSC data obtained from this series of polymers and percent crystallinities ($X_C$) and melting temperatures ($T_{m,PEO}$) for the PEO domain are summarized in Table 6.1. DSC data indicate increasing $X_C$ and $T_{m,PEO}$ as the volume fraction of O is increased indicating increased segregation of the PEO domains. In addition, $T_g$ of the S domain is much higher in ISI\textsubscript{30} ($T_{g,S} = 75$ °C) than ISI\textsubscript{19} ($T_{g,S} = 49$ °C) indicating segregation of domains even in the triblock precursor.
6.3 Results

Figure 6.10 (a) SAXS data on all ISI19 tetrablock with $f_0 \geq 0.22$ shows reflections attributed to a 2D hexagonal symmetry and (b) representative frequency sweep data is consistent with hexagonally arranged cylinders.

Figure 6.11 DSC endotherms for ISI30 (inset) and corresponding tetrablocks. Curves have been shifted vertically for clarity.
6.3 Results

**Figure 6.12** (a) Frequency sweep data for ISI30 displays scaling consistent with an ordered state. (b) SAXS data at 100 °C confirms a state of order in ISI30 which displays a sharp Bragg-like peak. In contrast, ISI30O-02 and ISI30O-04 are disordered at this temperature.

**ISI30, ISI30O-02, ISI30O-04.** All morphological characterization is performed above 100 °C, far from the observed glass and melting transitions, to avoid effects of vitrification or crystallization of individual domains. Frequency sweep data indicate ordering within ISI30 at 100 °C with $G' \sim \omega^1$ and $G'' \sim \omega^1$ (Figure 6.12a). This likely reflects lamellar order due to the symmetric nature of the triblock. However, higher order reflections of $(q/q^*) = 2$ and 3 are not observed within SAXS patterns (Figure 6.12b). The $2q^*$ may be missing due to structure factor extinction while the $3q^*$ peak falls outside the range of the SAXS detector. Comparing the SAXS patterns of ISI, ISI30O-02, and ISI30O-04 immediately reveals the Bragg-like nature of the ISI30 peak which is much sharper than the other two (Figure 6.12b). Clearly, increasing $f_O$ leads to a decrease in $T_{ODT}$ as both ISI30O-02 and ISI30O-04 display nearly terminal scaling at 100 °C in frequency sweep experiments as well. DSC results, which show a deviation from bulk $T_{g,S}$ as $f_O$ is increased, support the observation of a reduction in $T_{ODT}$ as $f_O$ is increased. While ISI30 displays a broad glass transition for the S block centered at 75.4 °C, ISI30O-02 has a $T_{g,S}$ of 64.6 °C. As O content increases, S and I domains start mixing to avoid the most unfavorable I/O contacts leading to a decrease in $T_{g,S}$. Glass transition of the S block
cannot be observed in samples with $f_O \geq 0.04$ due to the proximity of the melting temperature of the O domain ($T_{m,O}$).

**ISI$_{30}$O-06 and ISI$_{30}$O-10.** SAXS patterns of ISI$_{30}$O-06 annealed overnight at 100 °C show an underlying pattern of two broad peaks consistent with the ones seen in ISI$_{19}$O-07 and ISI$_{19}$O-10 (Figure 6.13a). However, Bragg peaks which can be indexed to BCC ordering are also clearly visible. Heating the sample results in a transition to the
6.3 Results

Figure 6.14 (a) SAXS pattern collected from ISI\textsubscript{30}O-21 display hexagonal symmetry at all temperatures and (b) frequency sweep data are consistent with a 2D hexagonal packing of cylinders.

Disordered state. DMS frequency sweep data was used to confirm the state of disorder at 110 °C and displayed terminal scaling of $G'$ and $G''$. Temperature ramp data on ISI\textsubscript{30}O-10 displayed a discontinuity around 170 °C upon heating indicating the possibility of an order-order transition (OOT) (Figure 6.13b). This tetrablock was annealed at 140 °C and 170 °C for one day, quenched in liquid nitrogen, and reheated to the annealing temperatures. SAXS patterns at 140 °C reveal two broad peaks as observed in ISI\textsubscript{19}O-07 and ISI\textsubscript{19}O-10. Heating the sample results in the appearance of additional Bragg-like peaks that can be indexed to the BCC phase (Figure 6.13a). Similar BCC patterns are observed in the sample which was annealed at 170 °C. Cooling the sample back to 140 °C and annealing for one week leads to a decrease in intensity of the Bragg peaks corresponding to BCC ordering (Figure 6.13a). TEM analysis is used to understand the ordering in these samples. Micrographs reveal that ISI\textsubscript{30}O-10 samples annealed for one day at 140 °C display spherical domains with no long-range ordering (Figure 6.13c), consistent with the SAXS patterns. In contrast, samples annealed at 170 °C for one day display clear regions of four-fold rotational symmetry (Figure 6.13d).
6.3 Results

**ISI30O-21.** SAXS patterns indicate the presence of 2D hexagonal symmetry in this sample (Figure 6.14a). Frequency sweep data show that $G'$ decreases steadily at intermediate frequencies, characteristic of cylindrical domains (Figure 6.14b). Based on analogous data from samples of similar $f_O$ in the ISI19 series, this sample is assigned the HEXC morphology over all temperatures tested. The sample does not disorder up to 240 °C and experiments beyond this temperature are avoided to prevent sample degradation.

6.3.3 Simulation results

As in the case of SISO, block segregation is difficult to conclusively establish based on DSC since $T_{g,S}$ is obscured by the melting endotherm of the O block. Even real space imaging through TEM is of little utility in this regard due to the limited staining options available. As a result, SCFT is once again used to provide critical insights into the state of segregation with specific focus on the effect of varying temperature. Here, it should be noted that SCFT is unable to exactly capture the $T_{ODTS}$ and $T_{ODTS}$ for the given samples because of extreme sensitivity to the exact functional form of $\chi(T)$. Nevertheless, this technique effectively elucidates distribution of polymer blocks across a unit cell in the sphere-forming BCC phase and qualitatively describes the effect of changing temperature on block segregation. Figure 6.15 illustrates simulated density profiles across the 1D [111] direction of closest packing in the BCC unit cell and in the 2D (110) plane. The 1D density profiles reveal that O is confined to the center of spherical domains, as expected. Despite the highest penalty associated with forming I/O interfaces, molecular architecture mandates adjacent placement of these domains. The interior I block forms a shell around the O domain while the terminal I block is resigned to mix with the S block and form the matrix. In fact, while the center of each domain is exclusively O, significant mixing is observed between the S, terminal I, and (to a small extent) the interior I domains at both temperatures as illustrated by Figure 6.15a.

Here, the SCFT calculations are carried out at 100 and 180 °C with the $\chi$ functions reported in Section 6.2.7. Figure 6.15a shows the emergence of sharper interfaces at the
Figure 6.15 SCFT simulated density plots for a tetrablock terpolymer corresponding to the molecular parameters of ISI19O-15 ($T_{ODT} = 188$ °C). Density profiles along the [111] direction in the BCC phase at (a) 100 °C and (b) 180 °C reveal the sharpening of interfaces at a lower temperature. This effect can be seen much more clearly in the simulated density plots corresponding to (c) 2D [110] planar cuts within the BCC phase. These highlight the density of each block at a low (100 °C) and high (180 °C) elucidating the mixing of domains as temperature is raised.
lower temperature and these differences are plainly highlighted by the 2D block density profiles shown in Figure 6.15b. The effects of increased segregation strength at the lower temperature are evident in the O domain; simulated density plots reveal a larger diameter of the sphere containing purely PEO. Upon lowering temperature, the S/I interfaces become increasingly faceted. Along the S/I interface, hexagonal faces of the BCC Wigner-Seitz cell (truncated octahedron) along the (110) plane are more pronounced at 100 °C as the matrix phase becomes increasingly segregated.

6.4 Discussion

On the basis of the preceding characterization, the ordered phases seen in symmetric ISIO tetrablocks are BCC and HEXC. As mentioned at the outset of this chapter, the goal of this work was to study the phase behavior differences arising from frustration alone. Contrary to the ABC triblock case, introducing frustrated interfaces did not lead to the stabilization of network forming phases. In fact, the phase behavior is quite “classical” displaying a transition from disorder to BCC packed spheres to hexagonally packed cylinders as \( f_O \) is increased. This sequence of observed morphologies reinforces the notion that these tetrablocks can be treated as pseudo [ISI]-O diblocks, especially near \( T_{ODT} \). Perhaps the most interesting finding relates to the phase characterized by two broad peaks observed in ISI_{19}O-07, ISI_{19}O-10, ISI_{30}O-06, and ISI_{30}O-10.

At first glance, scattering patterns obtained from these tetrablock samples compare favorably with those obtained from frustrated SIO (\( M_{n,SI} = 18.8 \text{ kDa}, f_S = f_I \)) triblock terpolymers between 0.043 \( \leq f_O \leq 0.086 \).\(^{131} \) These SIO triblocks also displayed two broad peaks with a similar intensity profile (Figure 6.16a). However, TEM characterization of the SIO triblock displayed no spherical domains and instead revealed a rectangular brick-like structure shown in Figure 6.16b. This phase was characterized as the pillared lamellar structure (PLS). It is clear from the TEM images presented here that domains observed in ISI_{30}O-10 are spherical. A second alternative for this phase is liquid-like packing of spheres (LLP), first observed in symmetric SISO tetrablocks around 0.07 \( \leq f_O \leq 0.09 \).\(^{141} \) This phase too is characterized by the appearance of two broad peaks. However, the secondary peak emerges at a \( q \) value
higher than the peak corresponding to the disordered SIS melt. This is in contrast to ISIO where, upon adding O, a second peak emerges at a lower $q$ value than the peak corresponding to the disordered ISI melt. The relatively high $q$ value indicates that O spheres are packed quite closely in SISO, consistent with the hypothesis that LLP is characterized by local tetrahedral coordination while possessing no long-range translation order. It is clear that the pattern observed here corresponds to neither PLS nor LLP.

The most intriguing feature of this pattern is the observed reversibility in ISI$_{30}$O-10. At lower temperatures, SAXS patterns show two broad peaks which give rise to additional Bragg reflections corresponding to BCC upon heating. If the sample is cooled from this state, peaks corresponding to BCC order disappear as shown in Figure 6.13a. This reversibility was not seen in the LLP phase and reversibility for the PLS phase was not characterized. We hypothesize this pattern results from melting of BCC order as the frustrated tetrablock attempts to transition to a phase of lower symmetry.

Analogous behavior was observed in poly(isoprene)-b-poly(lactide) (IL) diblocks where quenching a disordered sphere-forming melt ($T_{ODT,IL} = 48 \, ^\circ C$) to 40 $^\circ C$ resulted in growth of the BCC phase while quenching to 25 $^\circ C$ displayed growth of the $\sigma$ phase. Surprisingly, quenching the BCC phase to 0 $^\circ C$ (below the micelle-core $T_g$) results in a SAXS pattern consistent with disorder. The authors reasoned that transition to the
equilibrium σ phase from BCC likely involves a diffusion-less melting process which deletes any long range order within the system. This intermediate disordered state is trapped by vitrification of the micelle cores when the system is cooled rapidly to 0 °C starting from the BCC phase. It is possible an analogous effect is involved in the ISIO system. The BCC phase forms readily close to $T_{ODT}$ without the net exchange of mass but formation of the presumed lower-symmetry equilibrium phase at lower temperatures requires chain exchange between individual micelles. Here, high segregation strength (not core vitrification) due to the relatively high $\chi_{IO}$ halts chain exchange, causing the formation of a structure lacking any long-range order at lower temperatures. TEM micrographs help reinforce this idea; Figure 6.13c shows individual spheres that lack any translational periodicity. Heating the system results in the BCC phase, captured by the many regions of four-fold symmetry seen in Figure 6.13d. Thus, strong segregation resulting from the frustration condition prevents the formation of complex, low symmetry phases in contrast with the previously studied SISO system.

Simulated SCFT density plots support this conclusion by elucidating the optimal placement of chains in a BCC unit cell. We note again that the quantitative predictions of $T_{OOT}$ and $T_{ODT}$ are not rigorously accurate due to a pronounced sensitivity to $\chi(T)$. However, the density plots are instructive in qualitatively illustrating the nature of the segregation within the ordered phase as temperature is reduced. 2D density plots across the (110) plane of the BCC phase illustrate that each sphere adopts a core-shell geometry, as in the case of SISO. These findings are reinforced by DSC data which show a significant increase in O crystallinity as $f_0$ is increased, consistent with at least partial segregation of the I and O domains. The density plots also elegantly illustrate the arguments presented by Lee et al. about the role of sphericity in the formation of low-symmetry phases at lower temperatures. Briefly, as $T$ is reduced away from $T_{ODT}$, a sharp composition profile develops between the core (O) and corona (I) block. Therefore, morphologies whose Wigner-Seitz cells better approximate the spherical core-corona interface are favored in order to minimize distortions away from a spherical particle shape. Lower symmetry phases such as A15 and σ can accommodate this
constrain better than BCC. SCFT calculations elucidate the sharpening of S/I interfaces as temperature is lowered in the BCC phase while the core-corona (I-O) interface remains spherical. Due to the high penalty for chain extraction ($\chi_{IO} \gg \chi_{SO} \approx \chi_{IS}$), a lower symmetry phase is unable to form over the experimentally tested time scale (~1 week). Instead, the frustrated ISIO system melts from the BCC phase into a state with limited long-range order.

The effect of frustration on ODT is also seen here as previously demonstrated by Bailey et al.\textsuperscript{131} As seen in the transition from ISI\textsubscript{30} to ISI\textsubscript{30}O-02, $T_{ODT}$ initially decreases as O is added. This is due to the ability of S chains to shield the most unfavorable I/O contacts in the disordered state. Although the disordered state contains many more I/S contacts compared to the lamellar phase, the initial trend of $T_{ODT}$ suggests that this penalty is relatively smaller. The differences in ISIO vs. SISO phase behavior serve as a fascinating example of the effects of segregation strength in the formation of equilibrium structures. Switching to a frustrated ABAC architecture severely hampers mass exchange and prevents the facile formation of complex, low-symmetry phases.

6.5 Conclusions

This chapter described the synthesis and characterization of a series of linear and symmetric poly(isoprene)-$b$-poly(styrene)-$b$-poly(isoprene)-$b$-poly(ethylene oxide) tetrablock terpolymers. Two sets of ISIO tetrablocks were made by growing O from two symmetric ISI precursors of different molecular weights. These tetrablocks were used to study the effect of the frustration condition on a tetrablock architecture. The resulting ordered phases were BCC and HEX\textsubscript{C}. Absence of any complex sphere-forming phases was attributed to the high segregation strength which is a consequence of the frustrated nature of the I/O interface.

Acknowledgments. I greatly appreciate the help of Akash Arora in performing the SCFT simulations provided in this chapter. Dr. Kyungtae Kim was also very helpful in discussing the scattering data.
Chapter 7

Conclusions

7.1 Summary of Major Results

Continuing previous work,\textsuperscript{141–143,282} the phase behavior of SIS’O tetrablock terpolymers was investigated using a combination of DMS, SAXS, and TEM. Investigations were supported by SCFT calculations that identified a possible increase in the number of sphere-forming phases as the molecular symmetry parameter, $\tau = N_s/(N_s + N_{S'}),$ is adjusted. Motivated by these results and previous experimental investigation\textsuperscript{282}, eight SIS’O with $\tau$ ranging from 0.21 to 0.73 were synthesized using anionic polymerization and yielded experimental evidence for the presence of nine different sphere-forming phases: simple hexagonal (HEXs), FCC, HCP, BCC, rhombohedral (tentative), liquid-like packing, dodecagonal quasicrystal, and Frank-Kasper $\sigma$ and A15 phases. Tetrablocks with a relatively high molecular weight afforded access to deep quenches below the ODT while avoiding chain vitrification due to proximity to the glass transition of the SIS’ matrix. Studying these tetrablocks in detail yielded evidence for two distinct regimes. At temperatures close to the ODT, the tetrablock behave as pseudo [SIS’]-O diblocks and form equilibrium morphologies mediated by facile chain exchange between micelles. However, as seen in IL diblocks,\textsuperscript{92} further quenching led to a transition from equilibrium to non-equilibrium behavior at a
temperature approximately 20-30 °C below the ODT. We hypothesize that this transition is coincident with the loss of ergodicity as chain exchange is severely hampered due to increased segregation strength between the O core and SIS’ corona. SCFT calculations are used to elucidate the free energy landscape within the non-equilibrium structures from when $T < T_{\text{erg}}$ and suggest that the formation of phases within the non-ergodic regime is driven by rearrangement of the SIS’ matrix. These set of experiments demonstrate the importance of the $\tau$ parameter and temperature in the formation of ordered phases in this class of multiblock copolymers.

The previous experiments suggested a proclivity of low-\( \tau \) tetrablocks to form the HEXS phase. To the best of the authors knowledge, this phase has only been observed in tetrablock terpolymers\textsuperscript{143,289} and, thus, warranted further exploration. Experiments focused on SISO tetrablocks with $\tau$ values of 0.18 and 0.33, and $0 \leq f_{O} \leq 0.16$. TEM experiments were especially useful in identifying parallels between the transition from a cylindrical to a spherical morphology in diblock copolymers through an undulating cylinder intermediate as presented by Koppi et al. and the formation of the HEXS phase in tetrablock terpolymers.\textsuperscript{292} Though SCFT calculations are needed to confirm the proposed structure, we hypothesize that the HEXS phase is composed of hexagonally packed cylinder-like domains with embedded O cores that possess no periodicity along the cylinder axis. This leads to scattering patterns exhibiting hexagonal symmetry despite TEM experiments indicating the presence of spherical O domains.

As a compliment to the comprehensive studies on non-frustrated SISO tetrablocks, phase behavior studies were carried out on symmetric, frustrated ISIO tetrablocks where molecular architecture forces the formation of an interface between the two most thermodynamically incompatible I and O blocks. The frustration condition led to an extinguishment of the complex sphere-forming phase behavior observed in SISO tetrablocks; only HEXc and BCC ordered phase were observed within these tetrablocks. Switching to a frustrated ABAC architecture arrests mass exchange and prevents the facile formation of complex, low-symmetry phases. Despite the fascinating results obtained from multiple ABAC-type samples, the remaining eight enumerations of
tetrablock terpolymers offer tantalizing phase behavior possibilities. For example, Bates et al. hypothesized how ABCA'-type tetrablocks might form useful, non-centrosymmetric self-assembled structures such as Janus spheres. Towards this end, two synthetic strategies were presented that expand the monomer toolkit capable of producing ABCA-type tetrablocks with asymmetrically sized corona chains. A combination of anionic polymerization and ring opening transesterification polymerization (ROTEP) of (±)-lactide was used to synthesize LSBL’ while SIOS’ was prepared by a combination of anionic polymerization and reversible addition–fragmentation chain transfer (RAFT) polymerization.

7.2 Final Remarks

Self-assembly of sphere-forming block copolymers on complex atomic lattices has shown promise in developing photonic materials, nanoreactors, and drug delivery vehicles. Despite these practical applications, the most interesting facet of researching block copolymer phase behavior is the possibility of establishing unparalleled connections in self-assembly between seemingly disparate material classes. Although the prevalence of Frank-Kasper and quasicrystalline phases was recognized in metallic alloys decades ago, their discovery in soft materials is relatively recent. Studying the formation of these structures in a variety of materials such as surfactants, lipids, nanoparticles, and dendrimers has been instrumental in understanding the symmetry breaking involved in the formation of complex phases. Recent block copolymer research has been especially important in reinforcing links between packing modes in apparently unrelated materials. In particular, research on diblocks has revealed the nonequilibrium nature of certain quasicrystalline structures and surprising analogies in the role of sphericity and symmetric breaking that lead to the formation of complex phases in both hard and soft materials. The work presented here clearly demonstrates how a synergistic application of experiment, simulations, and theory will expand our understanding of periodic and aperiodic ordering, paving the way for understanding the fundamental principles guiding self-assembly across a wide range of materials and length scales.
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### Appendix

Table A1. Peak assignment and lattice parameters for the HCP, A15, and sigma phase observed in SIS′O-0.73.

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Table A.2 Peak assignment and lattice parameters for the HCP, A15, and sigma phase observed in SIS'O-0.68.

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