ABSTRACT

TALLURY, SRINIVASA SYAMAL SANMATH. Melt Spun Bi/Tri-Component Fibers Exhibiting Shape Memory: A Mesoscale to Macroscale Experimental and Theoretical Study. (Under the direction of Professor Melissa A. Pasquinelli and Professor Richard J. Spontak).

Formations of shape memory polymers (SMP) and soft smart structures that respond to the external stimuli have been in the forefront of polymeric materials development for the past three decades. Physical combinations of network forming and stimuli-sensitive macromolecular species ensure a highly versatile, scalable and cost effective means of creating SMPs materials. The incorporation of physically cross linked network formers not only allows excellent processing methods like melt spinning and injection molding, but also permits the structures thus formed to be reused and recycled. A sustainable route to achieving large scale production of SMP materials is explored by coprocessing linear low density polyethylene and poly-(styrene-co-(ethylene butadien)-co-styrene (SEBS) into bicomponent filaments. By controlling the composition, interfacial area and cross-sectional geometries of the bicomponent filaments, tunable SMP filaments were produced that respond to thermal activation. Bicomponent filaments composed of LLDPE/SEBS exhibit shape fixity at ambient temperatures due to the increased orientation in the homopolymer component resulting from plastic deformation. While the SEBS core component retains rapidly recoverable elastic strain. The recovery is observed to be spontaneous following the supply of heat that elevates the temperature of the LLDPE component and thereby making it mobile. Conventional shape memory behavior induced by heated programming is also possible in the bicomponent filaments and is investigated by means of thermal (differential scanning calorimetry), mechanical (tensile) and morphological(scanning electron microscopy) studies. The storage of macroscopic strain in the ambient temperature programming of SEBS/LLDPE
filaments is supported by studies on increase of crystalline and amorphous orientation using optical birefringence. The release of the shape after heating the filaments is rapid and mechanical and microscopic evidence points out the permanent loss of properties due to SMP cycling. The SMP behavior is quantified in terms of strain recovery and strain fixity ratios and is dependent upon the composition, interfacial area and intended maximum strain of the SEBS/LLDPE filaments. The stability of the interface even at high strains is identified as the key to maintaining shape memory performance of these bicomponent filaments. Mesoscale simulations using dissipative particle dynamics (DPD) were employed to study the microphase segregation and network formation in the triblock copolymers interfaces with homopolymers. Firstly, the adaptation of the simulations to the present coarse graining and implementation of a spatial clustering approach to quantify the fraction of chains existing as bridges, loops and dangling ends is discussed. Interfacial thickness, microphase segregation and network strength is studied with respect to varying incompatibilities among endblock, midblock and homopolymer species. In the simulation of experimental equivalent system, the fraction of bridges along the SEBS/LLDPE interface is estimated to linearly decrease with increasing PE volume content. Whereas the fraction of chains with both endblocks unsegregated increases rapidly from an insignificant number (0.05) at 50% to a large fraction (0.84) at 90% PE content by volume. Lastly, the investigation of molecular network formation in asymmetric triblock copolymers with increasing second endblock is conducted. A linear increase in the bridging and looping fraction with the asymmetry parameter is reported with a corresponding decrease in dangling ends.
Melt Spun Bi/Tri-Component Fibers Exhibiting Shape Memory: A Mesoscale to Macroscale Experimental and Theoretical Study

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Fiber and Polymer Science Materials Science and Engineering

Raleigh, North Carolina
2013

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DEDICATION

This is dedicated to my parents Ramarao and Girija Tallury and to my beloved wife Srivalli.

I cannot imagine my life without these persons playing their respective roles in it to make this intellectual journey possible. Although my father could not wait long enough to witness this day, he will always inspire me through his guiding words of wisdom. The most memorable are:

“Pride is a personal commitment. It is an attitude which separates excellence from mediocrity.” – William Blake

“There- my blessing with thee!
And these few precepts in thy memory
Look thou character. Give thy thoughts no tongue,
Nor any unproportion'd thought his act.
Take each man's censure, but reserve thy judgment.
This above all- to thine own self be true,
And it must follow, as the night the day,
Thou canst not then be false to any man.
Farewell. My blessing season this in thee!”

– William Shakespeare, Excerpts from Polonius’ Advice to Laertes, Hamlet I, iii
BIOGRAPHY

Syamal was born and brought up in Hyderabad (Andhra Pradesh), India. He is the only child to Ramarao and Girija Tallury and was named after his late grandfather (paternal). Syamal preferred and was encouraged to learn hands-on by active participation. After struggling with trigonometry and accounting in math, he one day happened to solve a quadratic equation by graphing it. Everything started to make sense after that discovery and Syamal began to enjoy calculus and constructed Bayesian mental models to explain real life occurrences. As early as in middle school (1996), Syamal enjoyed chemistry and physics and marveled the ubiquitous manifestation of physical chemistry concepts in daily life. His love for physical chemistry and hands-on learning survived through a lot of coerictions to choose different disciplines for undergraduate study. In his senior year (Osmania University; 2006-2007), Syamal worked under Dr. J.S.N. Murthy on two separate projects: one involving controlled drug release from hydrogels and the other involving glass fiber polymer composites using thermoset resins. He then started working (TECS, NC State University; 2007) with Dr. Melissa Pasquinelli on modeling CNT-polymer nanocomposites. He published most of his work in physical chemistry journals before joining the polymer morphology group (MSE, NC State University; 2010) as a co-advisee under Dr. Richard Spontak for his PhD. Syamal will be joining ExxonMobil Chemical Co. as a Polymer Research Scientist upon graduation.
ACKNOWLEDGMENTS

I am very fortunate to be associated with Professor Melissa Pasquinelli during my graduate education and I would like thank you for the unconditional support and encouragement you have given me over the past several years. You inspire me with your hard work, dedication, cheerfulness and most importantly with your optimism. I have learned many valuable lessons from you and continue to enjoy the privilege of being mentored by you. Looking back at my years at NCSU, I feel I am one of the most pampered graduate students. Thank you for everything!

I would like to thank Professor Richard Spontak for his guidance and support throughout my doctoral study. You are one of the best teachers I have encountered in my life and I think you are one of the few teachers who treat the pupils as equals and most importantly genuinely enjoy teaching. You have taught me to question every bit of my work, how to manage technical resources, to push my limits and to let my creative faculties loose. I have greatly benefited and enjoyed conversing with you over lunches and am a constant admirer of your patience and commitment.

I am grateful to Dr. Behnam Pourdeyhimi for facilitating my graduate education. You are a great inspiration to young scientists like me by exemplifying how to manage time, resources and facilities effectively. With your support and under your guidance I have had a unique chance to interact with some of the brightest minds in the polymer industry.

The insightful discussions I have had with Dr. Russell Gorga have greatly improved my understanding of polymers and their composites. I would like to thank Dr. Gorga for supporting and critiquing me on my masters as well as my doctoral thesis committees. I
would also like to thank faculty members at NCSU, Dr. Dale Batchelor, Chuck Mooney, Dr. Xiangwu Zhang, Dr. Warren Jasper, Dr. Stephen Michielsen, Dr. Donald Brenner, Dr. Melissa Bostrom, Dr. Michael Dickey, Dr. Alisson Motsinger-Reif, and Dr. Gary Howell for helping in my projects and in broadening my mind through intellectual discussions with you.

My lab mates Feng He, Jacob Majikes, Kenny Mineart, Enes Cakmak, Qian Jiang and Jing Chen have made my many days and nights in the laboratory livable. Special thanks goes to my friends Venugopal, Vijay, Ravikanth, Vamsi, Vishal and Lalith without whom I would instead be writing nonsense in a lunatic asylum. I also thank my collaborators Dr. Sidharth Thakur, Harish Chintakunta, Enes Cakmak, Qiang Jiang, Xin Wang, Chris Page for the many enjoyable conversations in the campus.

Finally, I would like to express thanks to my family in NC and back in India who have equipped me with the courage and will to embark on this intellectual journey. Special thanks to the Tallurys: Dr. T.S.B.N. Raju, Shyamalrau, Bharati, Shyamsundar, Sekhar, Madhavi and to the Manthas: Ramachandra rao garu, Annapurna garu, Mahesh, Mr. and Mrs. Satyanarayana garu and late Sri Bharadwaj. Thank you to Ram Mohan Rao garu, Gopal Kompally and Sriram Kiran Satyavolu to have extended me their timely support.
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Chapter 1

Introduction and Review of Literature

1.1 Motivation

“The most fundamental difference between compounds of low molecular weight and macromolecular compounds resides in the fact that the latter may exhibit properties that cannot be deduced from a close examination of the low molecular weight materials. Not very different structures can be obtained from a few building blocks; but if 10,000 or 100,000 blocks are at hand, the most varied structures become possible, such as houses or halls, whose special structure cannot be predicted from the constructions that are possible with only a few building blocks... Thus, a chromosome can be viewed as a material whose macromolecules possess a well-defined arrangement, like a living room in which each piece of furniture has its place.”

— Hermann Staudinger, quoted by Ralph Oesper in The human side of Scientists.¹

If matter was divided based on their internal energy ($U$) into hard and soft matter, soft matter represents the materials that interact with ambient conditions ($U \sim kT$, where $k$ is the Boltzmann constant, and $T = 300K$). Polymeric materials constitute a major part of soft matter along with living beings, foods, gels and other organic matter. The forces holding these ‘soft’ solids in place are relatively weaker and these can be reshaped by external stimuli such as mechanical and thermal energy.² The interaction among several forces of similar magnitude facilitates the existence of many metastable states in soft matter. This enables us
to engineer and apply structures that respond to relatively weaker stimuli available in everyday life.

Polymeric materials impact our lives to a great extent by simplifying and advancing the materials technology that surrounds us. The global plastics consumption is projected to reach close to 300 million ton by 2015 due to strong influence by the development of new applications and growing focus on green chemistry\textsuperscript{3}. A great amount of research has been focused on the development of polymeric materials to apply them as commodity plastics as well as specialty plastics. However, there is a limited growth in ‘intelligent’ and ‘stimuli-responsive’ polymer materials.

The motivation behind this work lies in developing scalable, sustainable, versatile and robust stimuli-responsive technologies based on polymeric materials. We envision that in the near future, there will be a revolutionary change in the inanimate objects, apparel, prosthetics, etc. that will make them interactive and responsive to their environment.

1.2 Shape-Memory Materials

Shape-memory materials possess the ability to assume one or more temporary deformed states and ‘remember’ its original shape upon the exposure to an external stimulus.\textsuperscript{4} While the shape-memory effect was first discovered in alloys,\textsuperscript{5} shape memory polymers (SMPs) comprise of a wide range of materials tunable to respond to various external stimuli.\textsuperscript{6,7}
1.2.1 Introduction to shape memory in polymers

Since their discovery in the 1980s\(^8\) shape memory polymers (SMPs) have captured a lot of interest.\(^4,6,9\) The SMPs are materials capable of undergoing large recoverable deformations under the application of an external stimulus.\(^10\) While most shape memory alloys rely upon reversible martensitic transformation as their triggering phenomenon, all SMPs possess two distinct structural features namely, the net-points and the switching segments.\(^6,11\) The net-points or the cross-links are responsible for the permanent shape of the SMP system whereas the switching segments hold the temporary shape. In thermally activated SMPs, the switching segments are characterized by a transition temperature (\(T_{\text{trans}}\)) above which the segments are mobile. The SMP is heated above \(T_{\text{trans}}\) and is fixed by dropping the temperature quickly at an induced deformation, thereby ‘fixing’ a temporary shape. When reheated above the \(T_{\text{trans}}\), their original permanent shape is recovered.\(^11,12\)

In addition to thermal activation, SMPs can be stimulated by electric and magnetic fields,\(^13\) light,\(^14\) moisture,\(^15,16\) chemical and pH stimuli\(^17\) etc. The main advantages of SMPs over their metallic and ceramic counterparts include high strains, low density, ease of processing and hence in tailoring the properties, programmability and control over recovery behavior etc. Most importantly SMPs can be produced at significantly low costs compared to metallic or ceramic alloys.\(^12\)

It is also possible to develop multi-functional SMPs and their composites.\(^9\) With the advent of nanotechnology, incorporation of nanoscale materials into SMPs has resulted in a wide array of applications of these materials.\(^7\) The latest developments enable SMPs to
accommodate the demands of a specific application such as biomaterials,\textsuperscript{18,19} sensors, actuators,\textsuperscript{7,11} etc. Recent applications of SMPs include space deployable structures (e.g., hinges and trusses), morphing skins used in folding wings in aircrafts, biomedical and biomimetic systems (e.g., vascular stent with drug delivery function, smart sutures), SMP textiles and self-healing systems.\textsuperscript{20}

Recent advances in the shape memory materials have led to the development of multiple shape recoveries in an SMP network.\textsuperscript{21,22} The networks are capable of recovering partially to a secondary temporary shape.\textsuperscript{23,24} Latest developments are even capable of multiple-shape memory effect where in several temporary states of the material can be captured en-route to the final recovery of the SMP network. For example, triple and quadruple shape-memory stimulated by temperature was demonstrated in Nafion.\textsuperscript{23} Such capabilities open new avenues for SMPs in the fields of deployable space structures, smart dry adhesives and as adaptive biomedical devices.\textsuperscript{20,7,25}

\textit{1.2.2 Fundamentals of Shape-Memory Polymers}

All SMPs are network structures and the crosslinking type and density controls the permanent shape of the material. Generally, SMPs consist of two components; while one component is highly elastic, another that is able to reduce its stiffness upon the application of a particular stimulus should be present. The reduction of stiffness may be caused by molecular phenomenon or by stimulus sensitive domains. Recovery in SMPs is caused upon
exposure to a certain stimulus when the strain energy stored in the temporary shape is released.

Most common SMPs are triggered by the application of thermal stimulus. Magnetic, optical and moisture triggered responses are also common. Figure 1 illustrates the macroscopic behavior of a thermally activated SMP during one cycle. The SMP materials is initially in its permanent shape ‘B’ and is depicted to be deformed due to the application of a load after heating above the $T_{\text{trans}}$. This temporary shape ‘A’ can be fixed by cooling down the material below the $T_{\text{trans}}$ rapidly. This step is called programming a deformation into the SMP. Reheating the SMP above the $T_{\text{trans}}$ is termed as recovery, during which process, the SMP returns to its original shape ‘B’.

1.2.3 Molecular Architecture in SMPs:

Polymeric materials exhibiting shape recovery require a molecular or supramolecular network that consists of long chains that define the initial shape.$^{20}$ The networks are stabilized by "binding" or "net" points, which remain intact upon exposure to the stimulus and thus enables memory of the initial shape. Therefore, the net points in a SMP network define the original shape and the chains connected by the net points impart the elasticity required for the deformed network to reacquire its initial shape after stimulation.$^{25}$ Shape-memory polymers also need at least one recovery elements, or switching segments, in the network that are capable of forming temporary interactions. The interactions between these switching segments are affected by the external stimulus.$^{7,17}$ The retention of temporary
shape and the transition to the original shape are determined by the stimuli-responsive switching segments. These switching segments thus determine the transition/stimulation conditions of SMPs.

Figure 2 delineates a schematic of the molecular mechanism responsible for the shape memory behavior. The netpoints are depicted as red dots whereas the switching segments are delineated as green (permanent) and blue (temporary) line segments. This is an example of SMPs with crystallizing segments. Shape-memory effect is brought about by a variety of other structures and their corresponding stimuli. Figure 3 summarizes the structures, stimuli and shape-memory functionality of some of the prominent shape-memory polymer materials.

It can be envisioned from Figure 3 that SMPs can be classified based on several different aspects such as composition, synthesis techniques, structure, type of stimulus and functionality to name a few. As the most common SMPs are thermally responsive and most commercial applications are concerned with the thermal activation of materials, thermally activated shape-memory materials are classified in detail below.

1.2.4 Classification of Thermally-Responsive SMP materials:

A schematic classification of the SMPs based on their structure is presented in Figure 4. Further classifications and a detailed structural description of each type are also given below. Shape-memory polymers are broadly classified on the basis of composition as four different types: 20

1. Covalently cross-linked glassy networks
2. Covalently cross-linked semi-crystalline networks
3. Physically cross-linked glassy copolymers
4. Physically cross-linked semi-crystalline block copolymers

**Covalently cross-linked glassy thermoset networks:**

These materials are composed of a cross-linked polymer network that exhibits a sharp glass transition temperature ($T_g$). They behave as elastomers beyond $T_g$, which can be tuned by varying the cross-link density and, in the case of bi/multicomponent systems, the composition. For example, a chemically cross-linked vinylidene random copolymer of poly(methyl methacrylate) and poly(butyl methacrylate) have $T_g$’s of 110 and 20 °C respectively. By varying the composition of these two species in the material, a sharp and tunable $T_g$ can be achieved for the resulting SMP network. Ultra-high molecular weight glassy polymer networks also can be considered as this type of SMPs as they do not flow above their $T_g$. These types of materials also show good shape fixity due to vitrification. Examples of such materials include high-molecular-weight poly(methyl methacrylate). Poly(alkyl methacrylate) copolymers, epoxy networks and amorphous polyurethanes constitute other examples of chemically cross-linked glassy SMPs.

**Covalently cross-linked semi-crystalline networks:**

Polymers in this category employ their inherent crystallinity to establish the conditions associated with shape fixing and memory. In this case, the melting temperature
(Tm) of the polymer effectively becomes the transition temperature for the SMP network. The permanent shape of these networks is established similar to that of the first category by chemical cross-links. Since melting is a first-order transition (unlike a glass transition, which is second order), the shape recovery is much faster as compared to the first case. The transition temperatures are also much narrower in range. These SMPs include bulk polymers that form phase-separated crystalline microdomains. Examples of materials in this category of SMPs include chemically cross-linked semi-crystalline rubber, polycaprolactone, and polycyclooctene.

Once initially shaped, the above two types of SMPs cannot be processed again into another shape or form. They also present significant challenges to recycling and reuse. Chemical cross-linking is introduced by site-specific reactions that form covalent bonds between neighboring chains and is therefore a stochastic phenomenon that can continue beyond the time of the primary reaction. The result is additional cross-linking and eventual embrittlement. Physically cross-linked networks developed on the basis of microphase separation or site-specific interactions (e.g., hydrogen bonding or electrostatic interactions) possess significant advantages over the previous materials for long-term end-use applications.

Physically cross-linked glassy copolymers:

These SMPs have unique advantages due to their rheological properties that facilitate melt processing using conventional thermoplastics technology. This class of materials is characterized by the presence of rigid, amorphous microdomains that serve as physical cross-
links. An excellent example of such materials includes microphase-separated block copolymers.\textsuperscript{37,38} These materials exhibit excellent recovery beyond the transition temperature and some varieties can be tuned even for biomedical applications.\textsuperscript{39} Another species is, however, required to introduce temporary shape fixation in the network through either crystallization or vitrification.

Other examples of such materials include polylactide copolymers,\textsuperscript{40} aromatic amide/polycaprolactone blends,\textsuperscript{18} polyamide/polycaprolactone blends\textsuperscript{41} and polyethylene terephthalate/polyethylene oxide blends.\textsuperscript{42–44} Polyurethane block copolymers exhibiting a sharp glass transition also belong to this category. Another example is the miscible blend of a segmented polyurethane with phenoxy resin and polycaprolactone.\textsuperscript{45} In addition of block copolymer systems, homopolymer blends such as those composed of poly(methyl methacrylate) and poly(vinylidene fluoride) can yield a melt-miscible system over all compositions.\textsuperscript{46} In this case, the poly(methyl methacrylate) is amorphous while the poly(vinylidene fluoride) crystallizes to serve as the source of physical cross-linking and likewise contributes to the modulus of the blend. The SMP transitions at the glass transition of the acrylic. Other physical associations such as hydrogen bonding and ionic clusters can also serve as physical cross-links.\textsuperscript{21,47} These cross-links exist in the hard segments of the networks and can be dissociated when melt- or solution-processing the polymer network. Such a material is reusable and can be reshaped multiple times.
Physically cross-linked semi-crystalline block copolymers:

In this case, the block copolymers contain a soft segment that is capable of crystallizing so that the melting point of this species establishes the transition of the SMP network. A classic example is the poly[styrene-b-(trans-butadiene)-b-styrene) triblock copolymer. The styrenic endblocks constitute 10-30 wt% of the molecule, and the system develops into a strongly-segregated network composed of the semi-crystalline polybutadiene midblock. Endblock-rich micelles exhibit a glass transition at 92°C (depending on block length), above which the copolymer can be melt-processed. The midblock on the other hand, melts at 68°C, thereby providing a 30º window for the shape-memory functioning of the copolymer.

An entire class of thermoplastic polyurethanes (TPUs) with semi-crystalline segments has evolved as excellent shape-memory candidates. These TPUs can be envisaged as multiblock copolymers with alternating hard and soft segments. The hard segments interact via hydrogen bonding, whereas crystallization of the soft segments is responsible for the transitioning phase. Addition of other species such as POSS-hybrid monomers can be used to induce segregation in the segmented polyurethane species. Crystallization of the soft segments introduces a secondary shape in the SMP network. These materials are of considerable interest due to their tunable stiffness and transition temperature and they are readily foamed.

One class of materials that deserve a special mention is liquid crystalline elastomers (LCEs). The wide range of combinations among mesogens and soft segment moieties
available for this type of chemistries enable a great way of tuning the shape-memory applications of LCEs.\textsuperscript{53-55} Ahir and coworkers\textsuperscript{56} have also been able to produce fibers with such materials. A series of studies on LCEs comprised of azobenzene units report the two-way light-sensitive shape-memory effect.\textsuperscript{57-59} The variation in alignment order propels the shape-memory in such LCEs. A detailed review on these materials by Ikeda and coworkers\textsuperscript{60} presents the versatility of LCEs in designing photoresponsive materials.

1.2.2 Quantifying Shape-Memory Behavior

Shape-memory behavior in polymers can be characterized by analyzing the mechanical response of the material on a stress-strain curve, as depicted in Figure 5. The signature response can be described in terms of four different steps as the network cycles through the loading.

1. The SMP is first heated above the transition temperature $T_{\text{trans}}$ and a load is applied. The first step therefore corresponds to a deformation $\varepsilon_m$ under a given applied stress.

2. The temperature is then lowered below $T_{\text{trans}}$ and the temporary shape is fixed in the network.

3. The load is withdrawn from the SMP and a strain $\varepsilon_u$ remains. A small strain is recovered due to chain relaxation.

4. Upon heating above $T_{\text{trans}}$ again, the material recovers its original shape. A permanent strain $\varepsilon_p$ is introduced into the system as a result of this cycle.
Two metrics are often employed to describe shape memory in polymers: strain fixity and strain recovery. These are defined below.

**Strain Fixity** $S_f$: This denotes the strain fixed in the temporary shape under a set of loading conditions and is given by

$$S_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}$$

where $N$ is the cycle number.

**Strain Recovery** $S_r$: This corresponds to the strain introduced in the recovered SMP after returning to its original shape and can be written as

$$S_{r,\text{tot}}(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m}$$

Thermoplastic elastomers are capable of excellent strain fixity, as well as strain recovery of above 95% under sustainable loading levels. Physically cross-linked networks as described as Type III and IV are also capable of moderately high deformation up to 200% strain.  

\[4,6\]
1.2.3 Emerging Directions in Shape-Memory Polymers

As emerging class of materials, SMPs find applications in a wide variety of applications ranging from in-vivo implants\textsuperscript{19,61,62} to outer space applications.\textsuperscript{17} Their low densities and large allowable deformations make them suitable for deployable components in aerospace. These applications include hinges, trusses, antennas, optical reflectors and morphing skins.\textsuperscript{7} While the tailoring of SMPs toward specific applications is intriguing, new avenues are emerging with the discovery of multi-functional SMPs,\textsuperscript{9} two-way reversible SMPs,\textsuperscript{63,64} structures capable of multiple transitions,\textsuperscript{22} and sustainable thermoplastic SMPs.\textsuperscript{24} In these directions we review a few important developments in multi-functional SMP materials.

1.2.3.1 Multi-functional SMPs

Polymer structures exhibiting triple shape memory were designed in the recent years by employing two separate domains with respective transition temperatures with chemically,\textsuperscript{65} and physically\textsuperscript{66} cross-linked network, with LCEs\textsuperscript{67} and with a bilayer approach.\textsuperscript{68} The chemical approach is exemplified by Behl and coworkers\textsuperscript{9} where a network comprising of PEG side chains with one end free to interact with a PCL network. A similar effect was obtained from linear or branched PE cross-linked with peroxide,\textsuperscript{69} and a more novel approach involving complementary hydrogen bonding in methacrylate copolymers.\textsuperscript{70} Physical approaches include polyurethanes with multiple crystalline phases such as two soft segments with different melting points.\textsuperscript{66} Bothe and coworkers\textsuperscript{71} employed POSS-PCL networks where the glass transitions of the segments were also utilized as the transition
temperatures for the triple shape memory. While LCEs route involved a side chain liquid crystalline network capable of two shape fixities via isotropic-nematic transition and glass transition, the bilayer approached utilized two epoxy SMPs bearing a wide gap between the glass transition temperatures reactively held together by curing one over the other.

Xie and coworkers first demonstrated a quadruple shape memory properties of perfluorosulphonic acid ionomer. Later the cycling behavior was reported to affect the SMP performance significantly. Another development from the same group employed Fe$_3$O$_4$ and CNT regions in an SMP composite system that can were stimulated at different radiofrequency ranges. Interpenetrating network system with a broad glass transition temperature range and a melting temperature was investigated by Li and coworkers.

With the expanding variety of the physical and chemical routes to devise SMPs, there are umpteen possibilities of realizing a future with commercial use of responsive polymer materials. But we believe that the development of scalable, sustainable, and cost effective alternatives will propel shape-memory polymers to the forefront of materials development for several decades in this century.

1.2.3.2 Shape-Memory Filaments and Textiles:

Textile and fibrous materials constitute a large portion of polymers material consumption. The value addition associated with textile applications and filamentous media drives many commercial and academic research groups toward innovation. Fibers with a wide range of diameters can be prepared to possess shape memory capability. Meng and
coworkers\textsuperscript{76} studied macro scale shape memory polyurethane filaments prepared from melt spinning as well as wet spinning techniques. They report better properties as well as efficient route of manufacture to be melt spinning of SMPUs. Kaursoin and coworkers\textsuperscript{77} investigated polyester-polyol based SMPUs under different drawing and heat setting conditions during melt spinning. Yet another group studied the effect of cationic group composition on the shape-memory behavior of polyurethane ionomers.\textsuperscript{78} Nanofibers of SMPUs were also reported to retain the shape memory effect.\textsuperscript{79}

Grafting of polyurethane on cotton\textsuperscript{80} and finishing applied on cotton\textsuperscript{81} were performed in an endeavor to transfer the shape-memory property to the cotton fabric/yarn. Membranes,\textsuperscript{82,83} and nonwoven webs\textsuperscript{84,85} were evaluated for shape-memory properties. Electrospun webs prepared from SMPUs were subjected to different studies for shape memory behavior.\textsuperscript{84,86,87} While nanofibers impart high surface area and enhanced functionality such as antimicrobial activity,\textsuperscript{88} the main promise in scaling up SMPs lies in developing macro/micro fiber materials capable of shape memory behavior.

Filaments produced via melt spinning of SMPUs exhibited excellent shape recovery properties.\textsuperscript{89} Other studies investigated for molecular orientation, recovery stress, and post-treatment on the SMPUs melt-spun filaments.\textsuperscript{90} A comparison of the mechanical and temperature response of SMP filaments with existing man-made fibers (Figure 6) reveals the superior performance of SMPU filaments. Meng and coworkers\textsuperscript{91} prepared SMPU hollow filaments (Figure 7) by using melt-spinning that can change the interior diameter based on the temperature. Electroactive SMP fibers containing carbon nanotubes and temperature-regulating smart fibers were also prepared by the same research laboratory.\textsuperscript{92,93}
Early developments in fabrics incorporated with SMP finishes\(^{81}\) reveal improvements in crease recovery.\(^{75}\) A schematic of the process is shown in Figure 8 and Figure 9 provides the shape memory recovery effects of the finished fabric.

### 1.3 Block copolymers as network formers

Block copolymers are comprised of segments of polymer chains connected along the backbone. When such segments are comprised of species that are incompatible with each other they phase segregate to form microdomains.\(^{94}\) The segregation of block copolymers and the resulting microstructures (Figure 9) are governed primarily by thermodynamic factors such as incompatibility between blocks, temperature and pressure and molecular architecture such as chain length and composition of the blocks.\(^{95,96}\) A wide spectrum of applications\(^{96}\) spanning from membranes\(^{97}\) to electroactive polymers\(^{98}\) utilize block copolymers as nanostructured base materials with unique properties. Block copolymers are often used to compatibilize polymer-polymer interfaces and improve adhesion.\(^{99,100}\)

Triblock copolymers of ABA type are given much importance as they form molecular networks capable of excellent mechanical strength and elongation.\(^{101-103}\) ABA copolymers are often used as network forms containing B-selective solvent to form a famous class of materials termed as thermoplastic elastomer gels.\(^{97,104}\) Recently, ABA copolymers with styrenic endblocks was utilized to prepare shape-memory materials and phase change materials in conjunction with paraffin waxes as the switching (midblock selective) component.\(^{105-107}\) Several studies in the literature investigated the homopolymer/AB copolymer interfaces\(^{108-110}\) and efficacy of AB copolymers in the compatibilization of A-B
However, for the case of ABA copolymer homopolymer blends, only low-molecular weight homopolymers have been studied.\textsuperscript{113–115}

Matsen\textsuperscript{116–118} and coworkers first addressed the network formation in ABA triblock copolymer systems via self-consistent filed theory calculations, predicted the Mattice and coworkers have employed Monte Carlo simulations to study the network formation in triblock copolymer systems under different conditions.\textsuperscript{119,120} Recently, dissipative particle dynamics were used to investigate the network formation in triblock copolymer melts\textsuperscript{121} and ABA systems with B-selective solvents.\textsuperscript{122,123} However, most of these studies assume a strong segregation regime for the AB incompatibility and a comprehensive understanding of the network evolution with the effects of compatibility and molecular weight is still necessary.
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Figure 1.1 Schematic of shape-memory materials responsive to heat.
Figure 1.2: Molecular mechanism of thermally responsive SMPs.$^6$
Figure 1.3: A summary of different structures, stimuli and functionality in SMP materials.25
Figure 1.4: Classification of thermally activated SMPs based on their structure.\textsuperscript{20}
Figure 1.5: Schematic representation of the stress-strain curve characteristic of a thermally-stimulated SMP network during cyclic loading.  

1. **Load**  
   \[ T_{\text{high}} > T_{\text{trans}} \]

2. **Cool (“fix”)**  
   \[ T_{\text{low}} < T_{\text{trans}} \]

3. **Unload**  
   \[ (T_{\text{low}} < T_{\text{trans}}) \]

4. **Heat (“recover”)**  
   \[ T_{\text{high}} > T_{\text{trans}} \]
Figure 1.6: a) Temperature response, b) Tensile response and c) Tensile response for first 100% strain of SMPU fibers compared with existing man-made filaments.
Figure 1.7: Hollow fibers made of SMPU shape-memory material that is able to change the internal diameter based on the exposed temperature.\textsuperscript{91}
Figure 1.8: (top) Schematic of SMP finish of on cotton fabric and (bottom) performance of crease retention in fabrics treated with SMP finish. \(^7\)
Figure 1.9: Theoretical phase-diagram of a diblock copolymer (top) and illustrations of the microdomain morphologies (bottom) with increasing volume fraction (f) of one block with respect to the other. The structures included are bcc spheres (CPS /Q229), hexagonal cylinders (H), cubic bicontinuous gyroid (Q230) and lamellar structures (L). The phase diagram is adapted from ref. 124.
Chapter 2

Melt-Spun SEBS/LLDPE Bicomponent Filaments Exhibiting Versatile Shape-Memory Behavior

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2.1 Abstract

This work explores physical means of achieving thermally activated shape-memory behavior in polymer filaments prepared using commercially available, cost effective materials as well as processing technique. The species contributing as a molecular network former (poly(styrene-co-(ethylene butylene)-co-styrene) is co-processed with a polyolefin (linear low density polyethylene) via bicomponent melt-spinning. The LLDPE participates as the switching species through two mechanisms 1. Conventional shape-memory behavior where LLDPE is softened and later cooled to program a temporary shape; and 2. Ambient temperature shape-memory where mechanical loading alone induces a stable temporary elongation due to increased molecular orientation. The two types of shape memory behavior are subjected to thermal, mechanical and morphological studies to explain the underlying mechanisms. The shape memory filaments thus produced possess excellent recovery ratios while capable of repetitive cycling with minimal loss of properties. Our work extends the

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boundaries of shape-memory material manufacture into physically designs that enable large scale production and application of shape-memory polymer filaments.

2.2. Introduction

Shape-memory polymers (SMPs) can assume one or more temporarily programmed deformed states until an external stimulus causes the materials to recover to their original shape.\(^1\,^2\) Thermally responsive SMPs are the most abundant manifestations of shape memory effect in polymers.\(^3\,^4\) Two features that are necessarily present in SMPs are a molecular network responsible for the ‘memory’ of the permanent shape of the SMP material; and at least one species capable of switching from rigid to mobile states depending on the application of an external stimulus.\(^5\) Several recent developments\(^6\) have combined different triggering mechanisms to create structures capable of dual\(^7\), triple\(^8\,^9\,^10\,^11\) and quadruple shape memory materials.\(^12\)

Several chemical approaches to achieving shape memory effect in polymers have been developed to be able to tune the response of the resulting SMPs.\(^13\) A variety of structures, stimuli responsible for triggering the shape memory and resulting functionalities were recently summarized by Hu and coworkers.\(^1\) While a large selection of materials and methods exist to tailor a SMP material to the conditions and properties demanded by a particular application,\(^4\,^14\,^15\) large scale application of SMPs in our day to day life is still far from reality. Limitations appear due to the complexity in the chemical processes required to produce SMPs, cost associated with the manufacture and issues concerning sustainable usage of materials.\(^16\,^17\)
Physical network formers stand out as viable alternatives to the above discussed limitations owing to their ability to reshape upon processing.\textsuperscript{18,19} Block copolymers in particular appear as excellent ordered materials capable of unmatched set of properties.\textsuperscript{20,21} Although many studies have focused on the inclusion of small molecular compounds in copolymer networks,\textsuperscript{22–25} the use of triblock copolymers in conjunction with homopolymers is relatively unexplored. Recent studies have utilized physical approaches to devise SMPs based on styrenic triblock copolymers and aliphatic oligomers.\textsuperscript{26,27} However, the processing techniques employed by these studies limit their scalable manufacture.

Scalable techniques such as melt spinning of polymers have been utilized before to produce shape memory filaments.\textsuperscript{28,29} Filaments with cross sections responsive to the temperature are also possible with this versatile technique.\textsuperscript{30} While the current knowledge of shape memory fibers permits the production of filaments capable of thermal shape memory,\textsuperscript{15,16} the substrates are restricted to shape memory polyurethanes (SMPUs). We again encounter a limitation on the scalability of such filaments due to the chemistry involved in the preparation of the SMPUs structures.\textsuperscript{31,32}

Our approach focuses on the combining materials capable of forming physically cross-linked molecular network and switching mechanisms in melt-spinning. Specifically, SEBS copolymer and a polyolefin (LLDPE) were subjected to bicomponent melt-spinning in core/sheath cross-sectional morphology respectively. We investigate the thermally activated shape-memory in thus formed filaments with a battery of characterization tools revealing the underlying mechanisms affecting the shape-memory performance. Such a route ensures easy processing, low cost, and the ability to tune the properties of SMPs by physical design.
2.3 Materials

The triblock copolymer (SEBS) used in this study is a well-known commercial polymer obtained from Kraton Polymers Inc. under the trade name of G1643 that is suitable for melt spinning. The copolymer chains contain 20 wt. % styrene and 80 wt. % ethylene butylene random copolymer. Whereas the polyolefin is a linear low density polyethylene (LLDPE) grade containing short side chains responsible for low crystallization in the homopolymer. The LLDPE was under the trade names Exxact 0230 from ExxonMobil Chemical Co. The homopolymer grades utilized in this study are suitable for injection molding.

Table 2.1. Details of the materials used for the bicomponent islands-in-sea spinning.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Commercial Name</th>
<th>Supplier</th>
<th>Density $^1$ $\rho$, g/cm$^3$</th>
<th>Softening Temperature $^2$ $T_m$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>Kraton G1643</td>
<td>Kraton Polymers Inc.</td>
<td>0.9</td>
<td>95.3</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Exxact</td>
<td>ExxonMobil Chemical Co.</td>
<td>0.9</td>
<td>70.5</td>
</tr>
</tbody>
</table>

$^1$ The density values for these polymers were obtained from the polymer data sheet supplied by the supplier.

$^2$ The softening temperatures of all polymers were estimated from differential scanning calorimeter at a heating rate of 10°C/min.
The materials included in this study are specific examples of polymers capable of being processed by melt-spinning while satisfying the condition that the switching component should soften well below the disruption of the physically cross-linked molecular network. We have performed the melt-spinning process at significantly lower speeds (300 m/min) compared to the commercial process in order be able to prepare samples uniformly. Negligible drawdown ratio was applied to limit the inline stress development in the spinning and winding processes.

2.4. Methods

2.4.1 Production of Bicomponent Sheath/Core and Sheath/Core₁/Core₂ Filaments

Filaments bearing sheath/sore cross-sections were produced on a Hill’s Inc. Bicomponent melt spinning machine whereas the tricomponent spinning machine by the same manufacturer was utilized to prepare sheath/core₁/core₂ filaments. The first set of filaments bear LLDPE in the sheath and SEBS component as the core of the filament cross section. The second set of filaments comprise of LLDPE in the sheath and core₂ (inner most) and SEBS as core₁. These filaments were obtained of each component to produce 20/80, 30/70, 40/60, 50/50, 60/40, 70/30 and 80/20 LLDPE/SEBS by volume ratio respectively (by controlling the melt pump ratios). The extruder temperatures were maintained at 210 °C, 220 °C, 230 °C, and 240 °C in the four zones for SEBS component and 190 °C, 195 °C, 200 °C, and 210 °C for the LLDPE component respectively. The filaments were collected about 1 meter below the quenching zone (maintained at 15 °C) by directly winding. The speed of
winder was set to collect at a similar rate as the filaments were spun and this rate was set constant at about 300 m/min.

2.4.2 Optical and Scanning Electron Microscopy

Scanning electron microscopy on the filament specimens was conducted on FEI Quanta 3D FEG microscope. In order to obtain the electron micrographs of each component, we have isolated the LLDPE component by dissolving the SEBS in toluene for 12 hours and drying the filaments in vacuum for 2 hours. We have freeze-fractured the filaments under liquid nitrogen to obtain cross sections of the filaments prior to the fastening the samples on the SEM stage. No sputter coating was applied on the filament samples to preserve the surface features that resulted from the spinning and to avoid thermal damage. The optical micrographs were obtained using Nikon Eclipse 50i POL optical microscope.

Optical Birefringence measurements were made using Becke Line method on the polarized light microscope. The refractive index media used were obtained from R. P. Cargille, Inc. (Cedar Grove NJ USA).

2.4.3 Differential Scanning Calorimetry

Thermal analysis of the bicomponent filaments and the polymer resins was performed on Perkin Elmer Diamond DSC calorimeter. Samples ranging between 4 to 5 mg were subjected to a heating rate of 10°C/min and in the temperature ranges from 25 °C to 200 °C. The melting and softening temperatures for the polymer species were obtained by analyzing
the calorimetry data for the average peak melting temperatures and glass transition temperatures from three different samples.

2.4.4 Thermo-Mechanical and Shape-Memory Testing

The shape-memory testing of the filaments was performed on TA Instruments Rheometric Solids Analyzer III. The samples were prepared from bundles of 80-100 filaments while maintaining the average cross-sectional area constant. The testing was conducted at different gauge lengths ranging from 5 to 50 mm, and a gauge length of 10 mm was chosen for consistency. Evaluating the shape-memory performance involved the measurement of strain stored in the temporary state as well as the recovered strain after heating the filaments. The testing procedure for conventional shape memory testing is as follows:

a) Start at a gauge length of 10 mm, heat the sample to 70 °C
b) Increase the load at a constant strain rate of 0.01 s\(^{-1}\) to reach a prescribed strain
c) Hold at the prescribed strain, quench the sample to 30 °C (programming)
d) Release the sample and measure the strain at a very small tensile load (~ 0.1 Pa)
e) Heat the sample to 70 °C and measure the strain under a very small tensile load
f) Repeat the above steps for successive cycles

For the shape memory testing with ambient temperature fixity, the testing methodology is as follows:

a) Start at a gauge length of 10 mm
b) Increase the load at a constant strain rate of 0.1 s\(^{-1}\)
c) Stop at the prescribed strain
d) Reduce the load until the stress reaches 0 MPa
e) Return to 0% strain or to the initial gauge length
f) Repeat the above steps for successive cycles (isothermal)
g) Heat the sample from ambient temperature to 70 °C at 20 °C/min
h) Cool the sample from 70 °C to ambient temperature at 20 °C/min
i) Repeat the above steps from step a) for successive recovery cycles

2.5. Results and Discussion

2.5.1 Morphology and Microstructural Analysis

The scanning electron micrographs of sheath/core and sheath/core\(_1\)/core\(_2\) filaments in the unstrained configuration are provided in Figure 1. The images of the cross-sections were obtained with only LLDPE component visible dissolving the SEBS component in toluene. The filaments in sheath/core and sheath/core\(_1\)/core\(_2\) cross sections are also visible in the longitudinal view. The overall diameter of the melt-spun filaments was observed to be uniformly distributed around 101.2±8.4 μm for the sheath/core and 99.7 ±9.3 μm for sheath/core\(_1\)/core\(_2\) filaments in the unstrained configuration.

The morphology of the filaments strained to 300% strain under ambient temperature conditions as well as those in recovered state (obtained after heating to 70 °C) are presented in Figure 2. There is a clear distinction in the morphology of sheath/core and sheath/core\(_1\)/core\(_2\) filaments in the deformed state under ambient conditions. Firstly, the
sheath/core filaments exhibit a microscopic surface morphology akin to shear banding (visible in the inset of Figure 2) wherein the sheath polymer undergoes large degree of orientation due to the plastic deformation past yielding. Macroscopically the filaments curl significantly. There diameter of filaments in this state is measure to be 58.6±6.2 μm indicating a 40% decrease in the direction transverse to loading axis. Sheath/core₁/core₂ filaments depict no such curling macroscopically but their diameter is reduced by 37% (62.8±4.5 μm). Such a distinction can be explained by the balance of stresses present in the innermost core (core₂) and the sheath components for the case of sheath/core₁/core₂ filaments. The absence of surface morphology indicates a uniform yielding with balanced strains along the radial direction of the sheath/core₁/core₂ filaments.

The recovered morphologies from the ambient temperature deformation of 300% strain are also provided in Figure 2. The sheath/core filaments recover to 96.2% of their original diameter whereas sheath/core₁/core₂ filaments show a recovery of 97.5% measured in terms of the microscopic diameter recovery. The surface morphologies occurring in the temporary state for the sheath/core filaments are absent after the recovery process. This suggests that the LLDPE component has reshaped itself after softening whereas the core component is causing the elastic recovery of the structure. A similar effect is seen in sheath/core₁/core₂ filaments.

Electron micrographs of the structures in temporary and recovered states for the conventional shape memory behavior are provided in Figure 3. Measurements from these structures indicate a microscopic recovery of 93.3% and 92.1% for sheath core and sheath/core₁/core₂ filaments respectively. The ratios compare lower to the ambient
temperature SMP behavior as the filaments undergo heated drawing that may contribute to a higher permanent set in the SEBS component as it is the only load bearing component during the programming step.

2.5.2 Conventional Shape-memory behavior of SEBS/LLDPE Bicomponent Filaments

Figure 4 delineates the shape memory behavior of thermally activated shape-memory behavior of SEBS/LLDPE filaments under heated programming with bundles of filaments. The strain, stress and temperature during the thermo-mechanical testing of 80/20 SEBS/LLDPE filaments is depicted using three different ordinate axes. The black (solid) curve depicts the strain of the material; red (dash) curve indicates the stress response in the filaments and the blue (short dash) curve indicates the temperature throughout the test. These three quantities are plotted on the ordinate axes whereas the time (seconds) is plotted on the abscissa.

The temperature (blue/short dash curve) starts at 70 ºC at which state the LLDPE component is mobile. After straining the first 170 s of the test at 0.1 s⁻¹, the temperature is ramped down to 30 ºC, thereby fixing the temporary shape in the filaments due to the solidification of the LLDPE component. The SEBS component is still in a network throughout this cycle and is currently in a strained state at about 170% strain. It is also observed that when the filaments are held at the strained state from 150 to 600 s, the stress drops as the LLDPE component solidifies. When the sample is let go at 600 s, the instrument tries to keep the sample taut while engaging the filaments in slight tension from 600 to 900 s. During the time, we can notice that the filaments are just taut (stress (red/dash) reaches zero)
at about 150% strain. As soon as the instrument oscillates above that particular strain, a corresponding stress is registered indicating that the filaments are engaged. The strain at which instrument equilibrates from 600 to 900 s is the temporary fixed strain as the LLDPE component is immobile at this stage. This means that the strain fixity of this sample is

\[ S_f = \text{Strain fixity} = \frac{\text{Unrecovered strain}}{\text{Maximum strain}} = 85.3\% \]

After 900 s in to the test, the temperature (blue/short dash) is increased back to 70 °C while maintaining a slight tension in the filaments to follow the material response. At this stage the LLDPE is mobile again, but the SEBS recovers the deformation very rapidly. Although it takes less than 2 s for the filaments to recover to a lower strain (black/solid curve past 900 s), the instrument is allowed to equilibrate and measure the strain recovery in the filaments. The measured strain recovery in the test is calculated by

\[ S_r = \text{Strain recovery} = \frac{\text{Strain recovered}}{\text{Maximum strain}} = \frac{170 - 26}{170} = 84.7\% \]

This procedure measures the shape-memory behavior of the filaments under heated programming for the first cycle. The filaments register strain fixity of 85.3% and a strain recovery ratio of 84.7%. The above thermo-mechanical cycle is repeated for 5 successive cycles to investigate the mechanical response following the initial deformation.
2.5.3 Effect of Maximum Strain and Cycling on the Conventional Shape-Memory Behavior

This shape-memory behavior was tested for different maximum strain levels of 70, 120 and 170%. Figure 5 depicts the evolution of strain ratios at the three different maximum strains with the increasing number of cycles for 60/40 SEBS/LLDPE filament in core/sheath cross-section. It can be noticed that the best shape memory behavior is observable at 120% strain. Overall the increasing cycles result in improvement of the SMP behavior due to more involvement of SEBS component. While strain fixity registers a minor increase during cycling, the strain recovery ratio is shown to have enhanced rapidly after the first SMP cycles. We investigated the effect of composition on the SMP behavior of the first cycle to further understand this behavior.

2.5.4 Dependence of Shape-memory Behavior on the SEBS/LLDPE Volume Ratio

Figure 6 captures the conventional shape memory performance for the first cycle of sheath/core1/core2 filaments as a function of the SEBS/LLDPE composition. The shape fixity ratios remained above 94% all through the compositional variation but no particular trend was observed as a function of the composition.

The recovery ratios however depict an increase from 30/70 to 40/60 LLDPE/SEBS volume ratio, beyond which there is a steady decrease in the recovery ratios reaching as low as 70% at 90/10 LLDPE/SEBS volume ratio. This trend suggests that the decrease in the molecular network content provides a small entropic and enthalpic incentive for the filaments
to retract. Moreover, higher compliance in the SEBS component allows the LLDPE to remain in the oriented state and fails to recover the filaments to their original shape.

2.5.5 Investigation of Ambient Temperature Shape-memory Behavior

In order to understand the ambient temperature behavior of the SEBS/LLDPE filaments we have subjected the filaments to cyclic mechanical loading under isothermal conditions (Figure 7a) followed by heating and cooling cycles (Figure 7b). There is a semicrystalline response in the filaments in the first loading cycle. It is clear that after the first loading cycle the filaments possess a hysteresis of about 32% of the maximum intended strain. The red curves (dashed) in Figure 7b indicate the response of the filaments after heating to 70 ºC and cooling to 30 ºC. The filaments recover to start loading from close to 0 strain after the first loading cycle past heating and cooling. It is evident that there is a loss in the mechanical property of the filaments in terms of the maximum stress and modulus. Yet there is a recovery associated with the sheath component that resets the loading to occur from 98% of the initial dimensions.

Optical birefringence measurements, provided in Figure 8a, indicate that the filaments possess increased orientation in the axial direction corresponding to increased amorphous and crystalline orientation in the filaments upon ambient temperature loading. However, a lot of this orientation remains in the filaments upon releasing (dashed curves in Figure 8a). The crystallinity was also found to increase by up to 6% in the case of 80/20 (LLDPE/SEBS by volume) sheath/core filaments. The appreciation in the crystallinity was found to be heavily dependent upon the LLDPE content as it is the only crystallizing component in the filaments.
This effect was similar in the case of sheath/core\textsubscript{1}/core\textsubscript{2} filaments except that even in comparable compositions of 50/50 and 30/50/20 there was a 3\% lower crystallinity associated with the sheath/core\textsubscript{1}/core\textsubscript{2} filament counterparts.

2.6 Conclusions

We have investigated the efficacy of thermally responsive shape-memory effect in filaments prepared by melt-spinning of SEBS and LLDPE with sheath/core and sheath/core\textsubscript{1}/core\textsubscript{2} cross-section. The filaments exhibited excellent spontaneous recovery within a second of heating to soften the LLDPE sheath component. Two types of shape-memory behavior namely via ambient temperature loading and conventional heated programming were discovered in the filaments. Conventional shape memory behavior was investigated at different compositions and the strain recovery was noted to drop rapidly with increasing LLDPE volume content in the sheath/core\textsubscript{1}/core\textsubscript{2} filaments beyond 50\% LLDPE. Further SMP cycles improved the strain recovery ratios by 14\% in the case of 60/40 SEBS/LLDPE filaments but the strain fixity ratios registered only a minor increase of within 2\%. The microscopic morphologies revealed interesting orientations in sheath/core cross section filaments, increasing curling resulted when released after room temperature loading. A radial balance of stresses in the sheath/core\textsubscript{1}/core\textsubscript{2} filaments eliminated this curling effect. The ambient shape memory effect is found to occur due to increased oriented amorphous and crystalline regions as evidenced by optical birefringence and calorimetry measurements as a function of strain. A robust physical design for shape memory filaments is demonstrated in a step toward developing commercially relevant SMP technologies.
2.7 References


Figure 2.1. Scanning electron micrographs of a) LLDPE sheath with scale bar representing 50 μm b) unstrained sheath/core with scale bar representing 100 μm c) LLDPE sheath and core₂ in sheath/core₁/core₂ filaments with scale bar similar to (a) and d) unstrained sheath/core₁/core₂ filaments with a scale bar similar to (b).
Figure 2.2. Scanning electron micrographs obtained for A) sheath/core filaments strained at room temperature B) recovered state from ambient temperature straining; C and D indicate sheath/core$_1$/core$_2$ filaments in strained and recovered states respectively.
Figure 2.3. Scanning electron micrographs obtained for (A) sheath/core filaments fixed at 70°C (B) recovered state from ambient temperature straining; (C) and (D) indicate sheath/core1/core2 filaments in strained and recovered states respectively. The scale bars are similar for left column and right column respectively.
Figure 2.4. Shape-memory behavior of 20/80 LLDPE/SEBS filaments with sheath/core cross-section at 170% maximum strain. The solid curve indicates strain, dashed curve represents stress and the temperature is plotted on a short dashed curve.
Figure 2.5. The strain fixity (solid) and recovery (hollow) ratios for conventional shape-memory behavior of 60/40 SEBS/LLDPE filaments with core/sheath cross-section at different maximum strains.
Figure 2.6. Strain fixity and strain recovery ratios for SEBS/LLDPE filaments with different volume ratios of SEBS/LLDPE.
Figure 2.7. a) Isothermal loading cycles of SEBS/LLDPE sheath/core filaments and b) isothermal loading (solid) followed by heating (70 C)/cooling (30 C) cycles.
Figure 2.8 a) Optical birefringence of SEBS/LLDPE filaments: the solid lines indicate measurements in the strained state and dashed curves indicate the measurement in the released state. and b) crystallinity measure from DSC as a function of strain for different compositions.
Chapter 3

Dissipative Particle Dynamics of Triblock Copolymer Melts: A Midblock Conformational Study

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3.1 Abstract

As thermoplastic elastomers, triblock copolymers constitute an immensely important class of shape-memory soft materials due to their unique ability to form molecular networks stabilized by physical, rather than chemical, cross-links. The extent to which such networks develop in triblock and higher-order multiblock copolymers is sensitive to the formation of midblock bridges, which serve to connect neighboring microdomains. Microphase-separated molecules can likewise adopt three other midblock conformations: loops, dangling ends and unsegregated chains. While prior theoretical and simulation studies have endeavored to elucidate the midblock bridging fraction in triblock copolymer melts, most have only considered strongly segregated systems wherein dangling ends become relatively insignificant. In this study, simulations based on dissipative particle dynamics are performed to examine the self-assembly and networkability of moderately segregated triblock copolymers. Utilizing a density-based cluster-recognition algorithm, we demonstrate how the simulations can be analyzed to extract molecular conformation information and permit

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explicit quantitation of the midblock bridging, looping, dangling and unsegregated fractions for ABA copolymers varying in chain length, composition and segregation.

3.2 Introduction

Due to their unique ability to spontaneously undergo microphase separation and self-assemble into a variety of soft, periodic nanostructures as a consequence of thermodynamic incompatibility,\textsuperscript{1-3} block copolymers continue to capture the attention of numerous fundamental studies and technological innovations. Triblock copolymers composed of hard (glassy or semicrystalline) A endblocks and a soft (rubbery) B midblock are of particular widespread interest from a commercial standpoint because they constitute thermoplastic elastomers (TPEs),\textsuperscript{4,5} a class of elastic materials that rely on the formation of molecular networks stabilized by physical, rather than chemical, cross-links. The molecular-level details of these networks will be discussed further below. Since their initial commercialization, TPEs have been commonly used in the large-scale manufacture of consumer products, ranging from automotive parts to sporting and household/office goods. More recent efforts have demonstrated that these versatile materials can be broadly incorporated into biomedical\textsuperscript{6} and microfluidic\textsuperscript{7} devices, vibration-dampening media,\textsuperscript{8} soft electroactuators,\textsuperscript{9,10} pressure-sensitive adhesives,\textsuperscript{11,12} shape-memory fibers,\textsuperscript{13} and large-strain flexible electronics.\textsuperscript{14,15} Unlike their chemically cross-linked analogs, TPEs can also be recycled and reprocessed through the use of either solvent or thermal means to avoid contributing to solid-waste pollution. From a fundamental viewpoint, ABA triblock copolymers, alone or in the presence of one or more small-molecule or polymeric additives, are interesting because they can self-organize into the same nanostructures\textsuperscript{16-19} (as well as
others\textsuperscript{20,21} observed in simpler AB diblock copolymer systems. The primary difference between the two copolymer genres lies in the ability of ABA copolymers to form molecular networks.

Previous experimental studies\textsuperscript{22-24} have explored the conformational transition from AB diblock to ABA triblock copolymer through the use of molecularly asymmetric A\textsubscript{1}BA\textsubscript{2} triblock copolymers grown from a parent A\textsubscript{1}B diblock copolymer. These efforts have demonstrated that the phase behavior, ordered nanostructure and mechanical properties exhibit a noticeably abrupt transition at a critical size of the progressively grown A\textsubscript{2} endblock. Complementary theoretical and simulation considerations\textsuperscript{25} reveal that this transition coincides with the formation of an equilibrium network composed of bridged midblocks, thereby establishing a direct connection between diblock and triblock copolymer archetypes. While this strategy has been recently extended to higher-order multiblock copolymers\textsuperscript{26} only molecularly symmetric ABA copolymers (with M\textsubscript{A1} = M\textsubscript{A2}, where M denotes block mass) are considered further in the present work.

Under strong-segregation conditions wherein the A and B blocks comprising an ABA triblock copolymer are highly incompatible, a copolymer molecule typically self-assembles in two ways, as depicted in Figure 1: (1) by depositing both of its endblocks in a single microdomain, thereby causing the midblock to adopt a looped conformation; or (2) each endblock in a neighboring microdomain, thereby causing the midblock to assume a bridged conformation. Numerous experimental\textsuperscript{17,27,28} and theoretical\textsuperscript{29,30} studies have sought to quantify the fractions associated with these conformations so that molecular conformations can be directly related to macroscopic (specifically mechanical) properties. In moderately
segregated systems, however, other midblock conformations, dangling ends (hereafter referred to as “dangles” and included in Figure 1), and unsegregated chains must be included in the population analysis.

In their seminal work, Mattice and co-workers\(^{31}\) have previously utilized Monte Carlo simulations to ascertain the fractions of bridges, loops, dangles and unsegregated ends (denoted here as \(f_L, f_B, f_D\) and \(f_U\), respectively, where \(f_L + f_B + f_D + f_U = 1\)) in ABA triblock copolymer-solvent systems and ABA copolymers confined between two parallel surfaces. In this work, we determine these fractions in moderately and strongly segregated ABA copolymer melts by employing dissipative particle dynamics (DPD), an approach akin to molecular dynamics simulations that combines a conservative force with viscous and random forces to facilitate the simulation of viscous matter.\(^{32}\) While DPD simulations have been used to investigate the self-assembly of diblock copolymers in prior studies,\(^{33-36}\) their recent application to network-forming triblock copolymer melts has been limited to strongly segregated systems,\(^{37,38}\) in which case \(f_B\) can be discerned explicitly from chain end-to-end distributions. Here, we demonstrate that a density-based clustering algorithm\(^{39}\) can be applied to analyze the trajectories from DPD simulations to extract the midblock conformational fractions for ABA triblock copolymers varying in segregation level, chain length and molecular composition.
3.3 Computational Methods

The coarse-grained particles (or beads) in DPD simulations are compressible and thus behave as soft spheres, which are linked together to replicate polymer chains as bead-spring equivalents. The net force \( F \) experienced by each bead during a DPD simulation is given by

\[
F = \sum_{j \neq i} \left( F^C_{ij} + F^D_{ij} + F^R_{ij} + F^S_{ij} \right)
\]

(1)

in which the summed forces account for all pairwise interactions between different beads (designated \( i \) and \( j \)) within a cutoff radius \( (R_c) \), which is commonly set to unity. The conservative (repulsive) force \( (F^C_{ij}) \) is written as

\[
F^C_{ij} = \begin{cases} 
\alpha_{ij} \left( 1 - \frac{r_{ij}}{R_c} \right) & \text{for } (r_{ij} < R_c) \\
0 & \text{for } (r_{ij} \geq R_c)
\end{cases}
\]

(2)

where \( \alpha_{ij} \) is the repulsion potential and \( r_{ij} \) is the distance between beads \( i \) and \( j \). Note that \( F^C_{ij} \) in Eq. 2 vanishes if \( r_{ij} > R_c \). The dissipative \( (F^D_{ij}) \) and random \( (F^R_{ij}) \) forces in Eq. 1 are defined as

\[
F^D_{ij} = -\gamma \ast W^D(r_{ij})(r_{ij} \cdot v_{ij})r_{ij}
\]

(3a)

and

\[
F^R_{ij} = \sigma \ast W^R(\theta_{ij})r_{ij},
\]

(3b)

respectively, where \( \gamma \) represents the viscous drag parameter, \( v_{ij} \) denotes the relative velocity between two beads, and \( \theta_{ij} \) is a randomly fluctuating term that obeys Gaussian statistics. The weighting functions \( (W^D \text{ and } W^R) \) are expressed as

\[
W^D(r_{ij}) = \left[ W^R(r_{ij}) \right]^2 = \begin{cases} 
(1 - r_{ij})^2 & \text{for } (r_{ij} < R_c) \\
0 & \text{for } (r_{ij} \geq R_c)
\end{cases}
\]

(4)

\[ \text{Note: } W^R(r_{ij}) \text{ is defined in Eq. 4 above.} \]
and the dissipative and random forces are related through the fluctuation-dissipation theorem by $\sigma^2 = 2\gamma k_B T$, where $k_B$ is the Boltzmann constant and $T$ denotes absolute temperature. (Note that this theorem naturally enforces a system thermostat.) Lastly, the spring force ($F_{ij}^s$) in Eq. 1 accounts for bead connectivity and is given by

$$F_{ij}^s = 8.0 \left(0.8 - r_{ij}\right).$$

(5)

In contrast to the other forces in Eq. 1, $F_{ij}^s$ is not equal to zero when $r_{ij} \geq R_c$ so that bead connectivity is maintained throughout the simulation.

A reduced system of units is employed in DPD simulations, and the unit of length in our simulations translates to 1.73 nm (the smallest cell we used has an edge length of 39.5 nm). All simulations have been performed using a microcanonical ensemble (constant mass, constant volume and constant energy), with the system thermostat set to 373 K, in which case $k_B T$ is set equal to unit thermal energy. Values of the number bead density, $\bar{\rho}$, and $\gamma$ are held constant at 3.0 and 4.5, respectively. The pair-repulsion parameters are calculated from group-contribution methods for the specific case of a triblock copolymer composed of styrene (A) and ethylene-co-butylene (B) moieties. According to Groot and coworkers, the value of the like pair-repulsion parameters ($\alpha_{AA}$ and $\alpha_{BB}$) is calculated to be 25.0 from $75/\bar{\rho} k_B T$. The cross parameter ($\alpha_{AB}$) is commonly calculated from $\alpha_{AA} + 3.27(1 + 3.9/N^{0.51})\chi_{AB}$, where $N$ is the number of beads per chain and $\chi_{AB}$ is the Flory-Huggins interaction parameter estimated from $V(\delta_A - \delta_B)^2/k_B T$. In this expression, $\delta_i$ represents the solubility parameter of species $i$ (where $i = A$ or B). These pure-component properties are accurately approximated for nonpolar species from group contribution methods to be $\delta_A =$
21.59 MPa\(^{1/2}\) and \(\delta_p = 16.97\) MPa\(^{1/2}\). In the current degree of coarse graining, \(V\), the volume of a DPD bead, corresponds to about 10 styrenic units (1000 cm\(^3\)/mol), or about 1.725 nm\(^3\), which is consistent with earlier DPD results from Maly et. Al\(^{25}\). Thus, for moderately segregated chains composed of 50 beads, \(\alpha_{AB}\) is calculated to be 48.3.

Initially random chain structures are generated from the chain.py routine in the LAMMPS computational package\(^{42}\) and then subjected to equilibration runs of 100,000 steps with periodic boundary conditions. Subsequent production runs are performed for 500,000 steps with a time step of about 2 ps in real time, thereby yielding a total run time of approximately 1 \(\mu\)s. Simulations have been conducted for systems containing copolymer chains systematically differing in length (\(N\)), molecular composition (\(f_A\)) and number. Here, \(f_A\) corresponds to the fraction of A beads in a copolymer chain and is varied to interrogate the role of morphology on network formation: spherical (\(f_A = 0.2\)), cylindrical (\(f_A = 0.3\)) and lamellar (\(f_A = 0.5\)).

Since single- and complete-linkage hierarchical clustering methods are either too sensitive to background noise or insufficiently sensitive to a broad range of existing clusters, we have elected to use a density-based clustering algorithm (DBSCAN\(^{39}\)) that ensures reachability while enforcing a minimum cluster size to systematically identify copolymer microdomains. This pattern-recognition algorithm is considered robust in a variety of contemporary applications, ranging from identifying broadband internet user time preference,\(^{43}\) lipid rafts in mixed lipid bilayers\(^{44}\) and objects in noisy video footage\(^{45}\) to elucidating chromatin interactions in genes.\(^{46}\) In general, DBSCAN commences by assuming that each bead lies in a different cluster. Two independent parameters are then used to
establish the existence of an actual cluster: $P_{\text{min}}$, the minimum number of observations required to classify a grouping as a legitimate cluster, and $\varepsilon$, the reachability that defines the span over which cluster-based linkages exist. If beads meet the conditions required by both parameters, they are allocated to the core of a cluster. If the conditions set by $\varepsilon$ are satisfied but those of $P_{\text{min}}$ are not, the corresponding beads are assigned to a cluster boundary. Beads that do not meet either condition are considered as noise and rejected from clusters. In terms of triblock copolymer melts, clusters correspond to endblock-rich microdomains, whereas the noise from snapshots of DPD simulations identifies beads belonging to the midblock-rich matrix (depending on the copolymer composition, since the morphology may consist of lamellae). In our adaptation, we force microdomains to obey periodic boundary conditions in all three dimensions by unwrapping bonded beads (along the endblock) if they cross a periodic wall in the simulation box.

3.4 Results and Discussion

3.4.1 Production of Microphase Morphologies

We first validate that the DPD simulations provide reasonable representations of the copolymer morphologies. The evolution of systems containing chains varying in $f_A$ can be followed up to $1.0 \ \mu s$ from time-resolved trajectories of endblock beads, such as those portrayed for $N = 50$ in Figures S1-S3 in the Supplemental Information (wherein the midblock beads are transparent). The ultimate microphase morphology (at $1 \ \mu s$) is provided in the left column of Figure 2 for increasing values of $f_A$. While the endblock beads are
initially positioned randomly throughout the simulation box in Figures S1-S3, noticeable organization is evident after the simulation progresses for just 0.1 \( \mu s \). At intermediate times, endblock beads diffuse further as the morphologies becomes increasingly refined and equilibrium is approached. In Figure 2 (left), A-rich micelles develop when \( f_A = 0.2 \). Although strongly-segregated block copolymer micelles are routinely positioned on a long-range body- or face-centered cubic lattice, the present simulation analysis displays a more loosely defined body-centered cubic symmetry. Moreover, the micelles are not always spherical. These differences in shape and extent of long-range order are attributed to the moderate copolymer incompatibility investigated at \( N = 50 \). At higher endblock compositions, well-defined hexagonally-packed cylinders (\( f_A = 0.3 \)) and alternating lamellae (\( f_A = 0.5 \)) are clearly observed after 1.0 \( \mu s \). A noteworthy feature of these relatively low-\( N \) simulations is that a nontrivial fraction of endblock beads remains located in the B-rich regions.

After ensuring that the simulations yield stable, representative copolymer morphologies at the conclusion of 1.0 \( \mu s \), we apply the density-based cluster algorithm to quantify the midblock conformations. In Figure 2, the final microphase morphologies from the DPD simulations (with \( N = 50 \) for 500 chains) after 1.0 \( \mu s \) are provided alongside the correspondingly delineated clusters from the DBSCAN algorithm, and favorable qualitative agreement is observed. In addition, individual endblock beads that do not belong to any cluster (and are considered noise) are included and colored in black. [Note: Regrettably, some clusters in the spherical and cylindrical morphologies also appear black.] Qualitative comparison of the panels in Figure 2 immediately divulges that the population of non-
clustered endblock beads, which are responsible for dangles and unsegregated chains, decreases systematically with increasing $f_d$. This observation is discussed further in the next section. Similarly, simulation trajectories and identified clusters for systems varying in size at constant $f_d$ (= 0.2) and $N$ (= 50) are presented in Figure S4. In this sequence of simulation/cluster results, the number of clusters within the isochoric simulation box, but not their size, is observed to increase with increasing system size, which is consistent with intuitive expectations. Due to microdomain crowding, however, it is difficult to visually distinguish the differently (and often repeatedly) colored clusters, as well as the non-clustered endblock beads (black). The DBSCAN clustering approach, however, enables a quantitative approach since it assigns a unique cluster number to each identified cluster. Thus, midblock conformations extracted from DPD-rendered clusters according to the criteria introduced earlier can be quantified as functions of chain length and repulsion potential (incompatibility), copolymer composition (morphology) and system size, as will be described in Section 3.3.

3.4.2 Parameterization of Density-Based Clustering

A significant challenge associated with using the DBSCAN clustering algorithm lies in choosing sensible values of $P_{min}$ and $\varepsilon$, which tend to be specific for an intended application. Chepelev and coworkers,\textsuperscript{46} for instance, have used DBSCAN to elucidate chromatin interactions in a genome. In their study, the optimal parameter values selected for identifying clusters are set equal to the number of detected intra-chromosomal paired-end-tag clusters that are significant at a false discovery rate of $< 5\%$. Thus, the first objective in the present
study is to develop a systematic approach by which to assign values of $P_{\text{min}}$ and $\varepsilon$ that are reasonable for our DPD simulations. To this end, we first examine the characteristic size of endblock-rich micelles (at $f_A = 0.2$) by calculating it from the radial pair distribution function, $g(r)$, which is defined as

$$g(r) = \frac{n(r)}{(\rho 4\pi r^2 \Delta r)} \tag{6}$$

where $n(r)$, the number of beads located up to a DPD distance $r$ is estimated from the volume of a sphere of radius $r$ with a bead density of 3 per unit volume. The average micelle diameter can be discerned at $g(r) = 1$, and the micellar period can likewise be estimated from the distance corresponding to the second maximum in $g(r)$. Comparison of the different $g(r)$ functions in Figure 3 for different chain lengths ($N$) and system sizes immediately reveals that both the microdomain size and period increase monotonically with increasing $N$, as expected, and that an increase in the size of the system has no discernible effect on the simulation results. In addition, the magnitude of the first maximum is also observed to increase with increasing $N$ due to the change in the number of bonded bead pairs.

The minimum cluster participation ($P_{\text{min}}$) value can be ascertained for each chain length on the basis of the findings displayed in Figure 3. Consider, for example, the case of $N = 50$. According to its $g(r)$ function, the micelle diameter measures $2.75r$, independent of system size (500 versus 2000 chains). The value of $P_{\text{min}}$ is therefore set equal to the corresponding number of beads occupying a micelle of this size, which is about 29 for $N = 50$. A similar methodology is followed to determine $P_{\text{min}}$ for the other copolymer compositions (morphologies), and the corresponding values of the micelle diameter and the number of beads/cluster are presented in Figure 4 as a function of $N$ for $f_A = 0.2$. 
Conversely, reachability values possess greater variability due to the intrinsically stochastic nature of the simulation trajectories. From each simulation run, the dependence of \( \varepsilon \) on the number of clusters counted is examined. This relationship, displayed in Figure 5 for \( N = 50 \) and \( f_A = 0.20 \), reveals that no clusters register above \( \varepsilon \approx 3.5 \) for 500 chains in Figure 5a or below \( \varepsilon \approx 0.13 \) for 1000 chains in Figure 5b. Although this parameter quantifies a range for the number of clusters, it contains no information regarding the size of the clusters. Since the size and uniformity of the clusters (microdomains) is more important than their number, we introduce the weight-average cluster size (\( S_w \)) as

\[
S_w = \frac{\Sigma_i n_i^2 x_i}{\Sigma_i n_i x_i}
\]

where \( x_i \) is the number of clusters possessing \( n_i \) beads per cluster. Figure 6 gives \( S_w \) as a function of \( \varepsilon \) for the same cases introduced in Figure 5. The inset in Figure 6 highlights the results in the vicinity of \( P_{\text{min}} \), which ensures at least 29 beads/cluster, and confirms that no clusters exist between \( S_w = 0 \) and \( S_w = 29 \). Each value of \( \varepsilon \) extracted from the corresponding point of intersection (0.15 for \( N = 500 \) and 0.19 for \( N = 1000 \)) represents the best system-specific choices to describe cluster reachability in the present DPD simulations. Thus, the values for \( P_{\text{min}} \) and \( \varepsilon \) that were used in the rest of this study (including Figure 2) are calculated for each case as per the radial pair distribution function without the need for any prior knowledge of the expected number of clusters.

3.4.3 Characterization of Network Formation

Since we developed a systematic and quantitative cluster-recognition protocol, the
uniquely identified clusters formed by the endblocks can then be analyzed in terms of network connectivity (Figure 1). A chain that participates in two different clusters, for instance, provides evidence of a midblock bridge. Alternatively, a midblock loop is identified when both endblocks reside in a single cluster. If one or both endblocks remain in a B-rich region (in no cluster), the midblock is considered a dangle or unsegregated copolymer molecule, respectively.

In the case of the spherical morphology ($f_A = 0.2$), Figure 7 provides the fractions of midblock bridges, loops, dangles and unsegregated chains displayed as functions of the number of beads per chain ($N$) and system size. These fractions are obtained from three independent runs, and an error bar measured at $N = 50$, which was observed to have the most variation in the simulations, is included in the figure to provide an overestimate of the standard error in the data. The system size, which ranges from 500 to 2000 chains, is observed to have little effect on the bridging fraction ($f_B$) from $N = 50$ to $N = 200$, whereas the looping fraction ($f_L$) is more sensitive to system size at low to intermediate values of $N$ when the system consists of only 500 chains. Interestingly, except for some small fluctuations at low $N$, $f_B$ is also relatively insensitive to $N$ over the range of $N$ examined. In contrast, both $f_L$ and the fraction of dangles ($f_D$) are more dependent on $N$: $f_L$ increases, while $f_D$ decreases, to plateau levels with increasing $N$. The onset of the plateaus for $f_L$ and $f_D$ occurs at $N \approx 100$. There is a small fraction of unsegregated chains $f_U$ at $N = 50$, but beyond $N = 75$ there fraction $f_U$ is negligible.

The extent of microphase segregation in block copolymers is dictated by the thermodynamic incompatibility, which is expressed as the product of the Flory-Huggins...
interaction parameter ($\chi_{AB}$) and, for linear copolymers, the number of statistical units along the copolymer backbone. In the limit of strong segregation, the blocks comprising each copolymer molecule are highly segregated and stretched normal to the interphase, and some morphological characteristics (e.g., the interphase thickness) become independent of $N$. If we presume that midblock conformations likewise become independent of $N$ in this limit, it follows that strong-segregation behavior first develops at the selected pair-repulsion parameter ($\alpha_{AB} = 48.3$) when $N \approx 100$, which translates into a molecular weight of about 100 kDa for a poly[styrene-$(b$-(ethylene-$co$-butylene)$)-b$-styrene] triblock copolymer. Below this value, dangling ends are more prominent at the primary expense of looped midblocks.

Since the networkability of TPEs via midblock bridging is largely responsible for their desirable property-governing characteristics, we now focus exclusively on $f_B$. The simulation results given in Figure 7 for copolymers self-organized into spheroidal micelles indicate that $f_B$ ranges from a system-average of 0.61 at low $N$ to about 0.59 in the strong-segregation regime. For the micellar morphology, previous efforts employing self-consistent field theory (SCFT)\(^1\), however, report a significantly higher value of $f_B$ (0.75 at an incompatibility of 40) at thermodynamic equilibrium. This nontrivial difference between prior SCFT predictions and our DPD simulations can be attributed to two reasons. The first is that DPD simulations represent copolymer chains that experience the same kinetic influences faced by real chains in the melt, whereas SCFT predictions yield a limiting value irrespective of the copolymer self-assembly pathway. This difference helps to explain why the morphologies displayed in Figure S1 do not exhibit perfectly-shaped spherical micelles arranged on a highly-ordered body-centered cubic lattice. While SCFT provides predictions in the limit of thermodynamic
equilibrium, many polymer systems never reach their lowest energy state due to kinetic barriers (e.g., vitrification) encountered as the chains seek equilibrium and endeavor to relax. In conjunction with this consideration, the DPD simulations explicitly account for the existence of dangles and unsegregated chains, whereas SCFT does not (and implicitly assumes \( f_B + f_L = 1 \)). We therefore contend that, while SCFT predictions provide an insightful, thermodynamic limit for \( f_B \), the value of \( f_B \) extracted here from DPD simulations, as well as the corresponding micellar size and shape distributions, may be more indicative of real copolymer melts. Such disparity is open to experimental interrogation.

As the block incompatibility depends on both the Flory-Huggins interaction parameter and chain length, an alternative route by which to explore the role of copolymer incompatibility on midblock conformations is by varying the pair repulsion parameter. In all of the results reported thus far, \( \alpha_{AB} \) has been held constant at 48.3. In Figure 8, the midblock conformational fractions in the limit of the micellar morphology are presented as a function of \( \alpha_{AB} \) ranging from 30 to 90 for 500 chains, each with \( N = 50 \). The lower limit on \( \alpha_{AB} \) is chosen due to the observation that copolymer chains evaluated at \( \alpha_{AB} = 25 \) remain fully phase-mixed. Even at \( \alpha_{AB} = 30 \), the simulations reveal a large population of dangles (0.46), and unsegregated chains (0.19) which is indicative of relatively poor microphase separation. As \( \alpha_{AB} \) is increased in this graph, however, both \( f_B \) and \( f_L \) increase to plateau levels (at 0.63 and 0.34, respectively), while \( f_D \) and \( f_U \) decrease to a negligible value when \( \alpha_{AB} > 70 \). It is interesting to note that \( f_B \) becomes independent of \( \alpha_{AB} \) when \( \alpha_{AB} \approx 50 \). Since \( f_L, f_D \) and \( f_U \) continue to evolve with increasing \( \alpha_{AB} \) beyond this value, we propose that unsegregated
chains and dangles prefer to transform into loops rather than bridges for body-centered cubic micelles. Comparison of Figures 7 and 8 also confirms that the transition to strong segregation in ABA melts is preceded by a nonlinear decay in \( f_D, f_U \) and a corresponding increase in \( f_L \). Since \( \alpha_{AB} \) is related to \( \chi_{AB} \), and \( \chi_{AB} \) generally depends on reciprocal temperature, it stands to reason that all three midblock conformations should change in opposite fashion from Figure 8 as the temperature is increased. This expectation is evident for the micellar morphology (\( f_A = 0.2 \) and \( \alpha_{AB} = 48.3 \)) in Figure 9, wherein \( T^* \) is systematically increased from 0.75 for 500 chains with \( N = 50 \). In this case, an increase in \( T^* \) introduces more random forces (Eq. 3b) and lessens the conservative forces (Eq. 2), thereby reducing the driving force for microphase separation as the order-disorder transition is approached. The results portrayed in Figure 9 are qualitatively similar to those obtained from on-lattice Monte Carlo simulations of molecularly asymmetric A\(_1\)BA\(_2\) triblock copolymers.\(^5\)

Although many triblock copolymers intended for use as TPEs possess a relatively small endblock fraction to ensure the formation of a dispersed morphology (i.e., spherical or cylindrical micelles) within a rubbery matrix, copolymer composition constitutes an important consideration since changes in morphology relate directly to variations in interfacial area. That is, the spherical micellar morphology possesses the highest interfacial area density of the classical morphologies. Interfacial area density decreases for the cylindrical and lamellar morphologies in that order, in which case we anticipate a systematic variation in midblock conformations. To test this hypothesis, values of \( f_B, f_L, f_D \) and \( f_U \) extracted from simulations conducted at \( \alpha_{AB} = 48.3 \) for 500 chains with \( N = 50 \) are displayed as a function of \( f_A \) in Figure 10. Included in this figure are ranges of \( f_B \) reported from SCFT
and experimental studies. While the trends are certainly comparable, the DPD results significantly underestimate these prior fractions evaluated for dispersed morphologies. Once again, we primarily attribute this difference to the presence of dangles, which account for about 10% of the midblock conformations in the spherical and cylindrical morphologies. Renormalization of $f_B$ and $f_L$ to eliminate $f_D$ and $f_U$ (so that $f_B + f_L = 1$) yields the results in Figure 10 that are in closer agreement with previous findings. As expected on the basis of considerations such as the interfacial area density, both $f_B$ and $f_U$ decrease, whereas $f_L$ increases, monotonically with increasing $f_A$. There is no significant change in $f_D$ with increasing $f_A$ relative to the measured standard deviation. Whereas, the reduction in $f_U$ most likely reflects enhanced microphase segregation as $f_A$ is increased (cf. Figure 8). In addition, the diffusion of endblocks to microdomains is facilitated in three dimensions (spherical micelles) relative to two dimensions (cylinders) or one dimension (lamellae). Trends similar to those included in Figure 10 have been observed by increasing $N$ to 75 and 100, but $f_U$ becomes increasingly negligible in those cases, which supports the renormalization-based comparison performed above.

3.4 Conclusions

Since thermoplastic elastomers constitute a fundamentally and technologically important class of soft materials, the objective of this study is to elucidate the midblock conformations of microphase-ordered ABA triblock copolymers varying in segregation and composition through the use of DPD simulations and a density-based cluster algorithm. We have found that the parameters employed during cluster recognition can be conveniently estimated from the radial pair distribution function of microdomain-forming beads, in which case no prior
knowledge of the cluster size or number is required. The DPD simulations performed here yield classic copolymer morphologies (i.e., body-centered cubic spherical micelles, hexagonally-packed cylinders and lamellae), which are then analyzed in terms of bead clustering to extract the fractions associated with the three possible midblock conformations: bridges, loops and dangles. These fractions are evaluated as functions of several important material/simulation considerations, namely, chain length, system size, bead repulsion, temperature, and copolymer composition. In all of these cases, the system size is determined to have relatively little effect on the midblock conformations, whereas systematic variations in chain length and bead repulsion reveal the onset of strong segregation (wherein the fraction of dangles is negligible). Quantitative comparison of the results obtained here with previously reported results for the midblock bridging fraction illustrates some discrepancy for the case of the dispersed (spherical and cylindrical) morphologies, which is most likely due to the exclusion of dangles in theoretical formalisms based on equilibrium thermodynamics. Because the clustering methodology employed here is systematic and robust, it can be applied to a wide range of triblock copolymer systems in which network formation is of considerable interest.

3.5 Acknowledgments

This study was supported by the Nonwovens Cooperative Research Center at North Carolina State University, grant number 10-127. We thank Professor Alison Motsinger-Reif and Mr. J. Majikes for technical assistance.
3.6 References


Figure 3.1. Schematic diagram of the possible midblock conformations of a microphase-ordered ABA triblock copolymer exhibiting a dispersed (spherical or cylindrical) morphology.
Figure 3.2. Microphase morphologies after 1 $\mu$s of DPD simulations for 500 chains with $N = 50$ at three values of $f_A$: (a) 0.2, (b) 0.3, and (c) 0.5. Top: Snapshots depicting the copolymer microdomains that are formed; Bottom: clusters identified by applying the DBSCAN density-based clustering approach to the corresponding simulations at the top, where each unique cluster is assigned a different color (that may repeat). Black beads (not in clusters) identify endblock beads that locate in midblock-rich regions. Note: some of the clusters also appear black.
Figure 3.3. Radial pair distribution function for DPD systems containing 500 copolymer chains varying in length \((N)\) at constant copolymer composition \((f_A = 0.2)\). The legend for \(N\) is provided in the inset, which is an enlargement of the boxed region to highlight the intersections indicated by arrows. Also included for the case of \(N = 50\) is a DPD system containing 2000 chains (bold dashed line). The solid lines serve to connect the data.
Figure 3.4. Micellar diameter (●) and the number of beads/cluster (○) determined from the radial pair distributions given in Figure 3 at constant copolymer composition \((f_A = 0.2)\). The solid lines serve to connect the data.
Figure 3.5. Number of clusters determined as a function of the reachability parameter ($\varepsilon$) for $N = 50$ and $f_A = 0.2$ for two DPD system sizes: (a) 500 and (b) 1000. Reproducibility is ensured from two independent runs: first (black) and second (red). The solid lines serve to connect the data.
Figure 3.6. Weight-averaged cluster size presented as a function of $\varepsilon$ for $N = 50$ and $f_A = 0.2$ for two DPD system sizes: 500 (circles) and 1000 (triangles). Reproducibility is ensured from two independent runs: first (black) and second (red). The inset is an enlargement of the data in the region corresponding to the cluster size estimated from the micellar diameter (dashed line). The solid lines serve to connect the data.
Figure 3.7. Dependence of midblock fractions ($f_B$, black; $f_L$, red; $f_D$, blue; $f_U$, magenta) on $N$ at $f_A = 0.2$ for DPD systems containing 500 (solid square), 1000 (open circle) and 2000 (open triangle) chains. The error bar corresponds to the standard error determined for the system with $N = 50$. The solid lines serve to connect the data.
Figure 3.8 Dependence of midblock fractions ($f_B$, black; $f_L$, red; $f_D$, blue; $f_U$, magenta) on the pair repulsion parameter ($\alpha_{AB}$) at $N = 50$ and $f_A = 0.2$ for DPD systems containing 500 chains. The error bars correspond to the standard error, and the solid lines serve to connect the data.
Figure 3.9. Dependence of midblock fractions ($f_B$, black; $f_L$, red; $f_D$, blue; $f_U$, magenta) on reduced temperature ($T^*$) at $N = 50$ and $f_A = 0.2$ for DPD systems containing 500 chains. The solid lines serve to connect the data.
Figure 3.10. Dependence of midblock fractions ($f_B$, black; $f_L$, red; $f_D$, blue; $f_U$, magenta) on $f_A$ at $N = 50$ for DPD systems containing 500 chains. Data renormalized to exclude the fraction of dangles are included as open circles. The grey regions indicate results from previous theoretical and experimental studies, and the solid lines serve to connect the data.
Figure 3.11. Snapshots of the DPD simulation showing the evolution of copolymer microdomains for the case of $N = 50$ and $f_A = 0.2$ at six different times (in $\mu$s): 0.0, 0.1, 0.3, 0.6, 0.9 and 1.0 (arranged left to right and from top to bottom).
Figure 3.12. Snapshots of the DPD simulation showing the evolution of copolymer microdomains for the case of \( N = 50 \) and \( f_A = 0.3 \) at six different times (in \( \mu s \)): 0.0, 0.1, 0.3, 0.6, 0.9 and 1.0 (arranged left to right and from top to bottom).
Figure 3.13. Snapshots of the DPD simulation showing the evolution of copolymer microdomains for the case of $N = 50$ and $f_A = 0.5$ at six different times (in $\mu$s): 0.0, 0.1, 0.3, 0.6, 0.9 and 1.0 (arranged left to right and from top to bottom).
Figure 3.14. Left side: snapshots of DPD simulations showing copolymer microdomains for systems varying in the number of chains – 500 (top), 1000 (middle) and 2000 (bottom) – at $N = 50$ and $f_A = 0.2$. Right side: density-based clusters identified in the corresponding DPD simulations and assigned different colors (which may repeat). Black beads (not clusters) identify endblock beads that locate in midblock-rich regions. Note: some of the clusters also appear black.
4.1 Abstract

In this study, dissipative particle dynamics (DPD) simulations are employed to investigate the phase segregation and interfacial characteristics of triblock copolymer/homopolymer blends in the melt. The three repulsion parameters corresponding to pairwise interactions among the two incompatible copolymer blocks and the midblock-selective homopolymer are systematically varied to explore the development of microphase morphologies (and their relative orientation), interfacial thicknesses and midblock conformations as functions of homopolymer selectivity and copolymer segregation strength. Complementary analysis of midblock conformations reveals that the fraction of bridge-forming copolymer molecules, which are responsible for network formation and system elasticity, decreases monotonically as the homopolymer volume fraction increases. The bridging fraction in the absence of homopolymer is predicted to be about 0.63 but drops to nearly zero in the presence of 90 vol% homopolymer. The results provided here help to elucidate the impact of both homopolymer selectivity and copolymer incompatibility on

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nanostructure development, chain conformation and interfacial adhesion.

4.2 Introduction

Since their commercial inception, block copolymers, each consisting of two or more long, chemically-dissimilar contiguous sequences that are covalently linked together to form a single macromolecule,\textsuperscript{1–3} have been used extensively in a wide variety of technologies,\textsuperscript{4} ranging from separation membranes\textsuperscript{5,6} and nanolaminate stabilizers\textsuperscript{7} to optical waveguides\textsuperscript{8,9} and electroactive media.\textsuperscript{10–12} As macromolecular surfactants in bulk systems,\textsuperscript{13} they are frequently used to improve the thermodynamic compatibility of immiscible polymers by lowering the interfacial tension along the polymer-polymer interface.\textsuperscript{14–16} Doing so is intended to improve the interfacial adhesion and fracture toughness of the resulting blend, as well as its long-term stability and cycle life.\textsuperscript{17–20} Related efforts have focused on block copolymers in the presence of a single block-selective homopolymer to discern not only the conditions yielding macrophase separation but also the effect of imbibed homopolymer on copolymer morphology. While most studies of blend compatibilization\textsuperscript{21,22} and homopolymer-induced copolymer modification\textsuperscript{23–26,27} involve diblock copolymers, several have addressed\textsuperscript{28,29} block copolymers having other molecular architectures. Of particular interest in the present work are molecularly-symmetric, bicomponent ABA triblock copolymers. These materials are often designed with glassy or semi-crystalline endblocks and a rubbery midblock, and behave as thermoplastic elastomers (TPEs).\textsuperscript{30} As such, they (and other architectures\textsuperscript{31} that likewise possess a rubbery midblock) are capable of forming midblock bridges and, hence, a molecular network that can impart mechanical elasticity.

Several efforts have examined the morphology and properties of microphase-ordered
ABA copolymers swollen with a low-molecular-weight, midblock-selective homopolymer (hB) and have established the conditions leading to morphological transitions and property variation. Surprisingly, however, a detailed molecular-level analysis of the interactions between ABA copolymer molecules in the presence of hB, coupled with associated morphological and network development, remains lacking. For the purpose of interrogating the bulk and interfacial characteristics of ABA/hB blends, we turn our attention to computer simulations. For instance, a recent study utilizing dissipative particle dynamics (DPD), a molecular dynamics approach that combines conservative, viscous and random forces to simulate viscous matter at mesoscale dimensions, has probed the evolution of interfacial roughness in polymer-polymer blends. Similarly, DPD simulations have been successfully used to interrogate the formation of vesicles and membranes, the stability of monolayers and the dynamics of polymer solutions. Key developments in the methodology also permit application of DPD simulations to microphase-separated block copolymers. More specifically, these simulations have helped to elucidate the phase behavior and dynamics of ABA triblock copolymers, as well as the onset of network formation in molecularly-asymmetric A1BA2 triblock copolymers. As far as we are aware, no DPD simulations reported thus far have focused on characterizing the interfacial characteristics of ABA/hB blends.

In an accompanying experimental study, we have developed novel shape-memory materials composed of bicomponent fibers wherein a TPE core that provides the elastic network required for shape recovery is melt-welded to a midblock-compatible, thermoplastic sheath that affords the external stimulus ("trigger") via crystal melting. Thus, the principal
objectives of the present DPD simulations are two-fold: (1) ascertain how and the extent to which the morphology of a microphase-separated ABA copolymer is affected by hB penetration at different copolymer and block/homopolymer incompatibility levels, and (2) determine the corresponding network integrity, as signified by the midblock bridging fraction, under the same conditions. These results will provide a molecular-level perspective of the interfacial characteristics of ABA/hB blends.

4.3 Simulation Methodology

To discern the role of midblock-selective homopolymer on the morphological and network development in ABA triblock copolymers, we performed two complementary series of DPD simulations. In the first series, the interactions of nondescript copolymer and homopolymer chains of constant length were systematically varied, whereas ABA/hB blends explicitly matched to our experimental studies were considered in the second series. The DPD methodology utilized here is similar to that described elsewhere and is briefly summarized here. Each simulation run was performed with the LAMMPS simulation package. For conventional blends, the initial copolymer and homopolymer chains were randomly placed inside the simulation box. Conversely, chains purposefully positioned as planar copolymer and homopolymer "sheets" in contact were designed to emulate melt welding, but yielded results that compared favorably with the analogous blends. In all cases, several simulation conditions were held constant: the self-repulsion parameter ($\alpha_{ii}$, where $i = A, B$ or $H$) was set to 30 at a bead density ($\bar{\rho}$) of 3.00 DPD beads/(DPD unit)$^{3}$ and an absolute temperature ($T$) of 373 K. Harmonic forces between beads were represented by $F_H =$
\[ 4.0(r - r_0)^2 \], where \( r \) and \( r_0 \) denote the instantaneous separation between the two particles and the equilibrium bond length, respectively, and the beads were coarse-grained in such fashion so that 1 DPD bead \( \approx 10 \) styrene repeat units (\( 10^3 \) Da). All simulations, conducted on the 24 parallel processors comprising the NCSU High-Performance Cluster (HPC), started with a 10,000-step equilibration run followed by a 500,000-step production run.

### 4.3.1 Details of the Simulation Series

The ABA/hB systems examined here consisted of 2,000 ABA chains and 2,000 hB chains in which each chain contained 50 beads, thereby yielding ensembles containing a total of 200,000 beads. The simulation box was a cubic cell with each edge measuring 40 DPD length units (which translates to \( \approx 75 \) nm), and periodic boundary conditions were maintained in all three directions. As mentioned above, the equilibrated ABA/hB morphologies were found not to be sensitive to initial chain placement. The three pairwise repulsion parameters labeled in Figure 1 (\( \alpha_{AH} \) between A blocks and homopolymer, \( \alpha_{BH} \) between B blocks and homopolymer and \( \alpha_{AB} \) between A and B blocks) were systematically varied to quantify the effect of segregation strength on morphological and network characteristics. For clarity, these parameters will be hereafter listed for each simulation according to the convention \( \alpha_{AH}/\alpha_{AB}/\alpha_{BH} \), and an increase in the magnitude of \( \alpha_{ij} \) corresponds to an increase in segregation strength. If the A beads cannot distinguish between the B or homopolymer beads, then \( \alpha_{AH} = \alpha_{AB} \). If, however, the A beads prefer to interact with the homopolymer beads than the B beads, then \( \alpha_{AH} < \alpha_{AB} \) and vice-versa. Specific values selected for the pairwise repulsion parameters used here are provided in Table 1. On the basis of an independent study (refer
Chapter 3) devoted exclusively to the molecular characteristics of neat ABA melts, the incompatibility between the copolymer endblocks and the homopolymer (\(\alpha_{AH}\)) is anticipated to play a crucial role in microphase separation and physical network formation in the copolymer/homopolymer blends. Simulation data acquired from 3 independent runs have been averaged to yield the results presented in following sections.

A second series of simulations focused on copolymer/homopolymer pairs used in a companion experimental study of shape-memory bicomponent fibers. The selected copolymer was a poly[styrene-\(b\)-(ethylene-co-butylene)-\(b\)-styrene] (SEBS) triblock copolymer, whereas the polyolefin homopolymer was linear low-density polyethylene (PE). These three homopolymers were chosen because they represent different levels of interfacial adhesion with the copolymer, ranging from good to poor. For cases with moderate-to-good adhesion, the simulations consisted of 50,000 beads and a total of 1000 chains. Several representative simulation cells were constructed by knowing the composition profile along the ABA/hB interface. The volume fraction of homopolymer was varied from 0.0 to 0.9 in increments of 0.1 to simulate the composition profile normal to the ABA/hB interface. The pairwise repulsion parameter between like beads (\(\alpha_{ii}\)) was held constant at 25, whereas the repulsion parameter between dissimilar beads (\(\alpha_{ij}\)) was obtained from

\[
\alpha_{ij} = \alpha_{ii} + 3.27(1 + 3.9N^{-0.51})\chi_{ij}
\]

where \(N\) is the chain length in terms of DPD beads and \(\chi_{ij}\) is the Flory-Huggins interaction parameter. Since the chemical species comprising the simulation are nonpolar, \(\chi_{ij}\) can be accurately estimated from solubility parameters according to
where $V$ represents the volume of one DPD bead ($\approx 1000 \text{ cm}^3/\text{mol}$), $\delta_i$ denotes the solubility parameter (i.e., the square root of the cohesive energy density) of species $i$, and $R$ is the universal gas constant. The cohesive energy density of each species is estimated from Fedors group contribution method, and values of the resultant repulsion parameters are provided in Table 2.

4.3.2 Analysis of Simulation Results

Since $\bar{\rho} = 3$ DPD beads/(DPD unit)$^3$, the interface was classified as the region over which the copolymer and homopolymer composition profiles exhibit a lower density. Thus, density profiles of the species in each simulation were generated by binning the beads along slices measuring 1 DPD unit thick normal to the interface. The corresponding interfacial thickness was determined by fitting the density profile, $\rho(x)$, to a hyperbolic tangent function of the form

$$\rho(x) = \frac{\bar{\rho}_{\text{max}}}{2} ((\tanh mx + k) + 1)$$

where $\bar{\rho}_{\text{max}} = \bar{\rho} = 3.00$ beads/(DPD unit)$^3$, $x$ is the position of the profile along the interfacial normal, $k$ is the offset of the interface within the simulation box, and $m$ is a scaling factor that depends on the segregation strength and governs the sharpness of the interface. The interfacial thickness ($\lambda$) is therefore defined as the distance between $x_1$ and $x_2$ at which $\rho(x_1) = 3.00 \pm 0.01$ and $\rho(x_2) = 0.00 \pm 0.01$ beads/(DPD unit)$^3$, respectively. In addition to
quantitatively describing the interfacial characteristics of ABA/hB blends, we also investigated network properties as functions of different pairwise repulsion parameters and position along the interfacial normal. The molecular network formed by microphase-ordered triblock copolymers depends largely on the fraction of midblock bridges present. As depicted in Figure 1, a bridge is defined as a copolymer molecule that deposits its endblocks in two different A-rich microdomains, whereas a loop occurs when both endblocks reside in the same A-rich microdomain. Two other possibilities that must be considered are dangling ends (with only one end in an A-rich microdomain) and unsegregated chains (with no endblocks in A-rich microdomains). The fractions representing these midblock conformations – $f_B$ (bridges), $f_L$ (loops), $f_D$ (dangling ends) and $f_U$ (unsegregated) – are used here to characterize the physically cross-linked network. These fractions were calculated by first identifying the A-rich microdomains with a density-based clustering algorithm and then counting the participating chains.

4.4 Results and Discussion

The two series of simulations performed in this study are designed to ascertain the interfacial characteristics and network properties of blend composed of ABA triblock copolymer molecules and midblock-selective homopolymer molecules. In the first series, the blend composition is fixed at 50/50 v/v ABA/hB, and the copolymer composition is held constant at 20% A. While this copolymer composition is lower than that of most commercial TPEs (at 30-33% A), it is close to the composition of the copolymer used in our companion experimental study of shape-memory fibers. The pairwise repulsion parameters in the first
simulation series are varied systematically to ascertain the effect of segregation strength on morphological and network characteristics. The second series of simulations corresponds closely to experimental blends.

4.4.1 Results from the Systematic Series

The pairwise repulsion parameters accounting for endblock/midblock and endblock/homopolymer interactions ($\alpha_{AB}$ and $\alpha_{AH}$, respectively) govern microphase separation of the copolymer and macrophase separation of the two polymeric species. They are also responsible for network development and accompanying mechanical attributes as they dictate the extent to which the copolymer molecules form bridges. At the three levels of copolymer incompatibility examined ($\alpha_{AB}$ ranges from 30 to 90 DPD units in increments of 30 DPD units), values of $\alpha_{AH}$ are varied from 50 to 90 in increments of 10 DPD units (cf. Table 1). In general, all of the systems display unequivocal evidence of macrophase separation, which agrees with intuitive expectation. It is, however, interesting that two different types of macrophase-separated morphologies are observed: one in which both phases are dispersed (D,) and the other in which both phases are planar (P, Table 4). While clearly delineated phases are evident in both cases, the interfaces that develop in the dispersed macrophase morphologies tend to appear rough, which hinders further analysis. With regard to the copolymer morphology within these systems, three distinct scenarios are likewise apparent (as shown in Tables 3 and 4). In one example, the copolymer blocks remain completely unsegregated (U), whereas the endblocks self-assemble to form micelles (M) or cylinders (C) in the other two instances. To describe these hierarchical morphologies, we label them as
XY, where X refers to the macrophase morphology (D or P) and Y describes the microphase morphology (U, M or C).

Since the M morphology is cubic and the unit cell is oriented parallel to the interface, an orientation is not assigned to this morphology. The C morphology is, however, anisotropic and we find that the cylinders can arrange either parallel (||) or perpendicular (⊥) to the interface separating the coexisting polymer phases. The morphologies of ABA/hB blends not included in Tables 3 and 4 are provided as Supplemental Information. In blends exhibiting a well-defined P macrophase morphology with a relatively flat interface, composition profiles of each species normal to the interface can be determined as described earlier. Examples of such profiles, which correspond to the simulation results shown in Table 4, are presented in Figure 2 and compare favorably with the interfacial composition profile given by Eq. 3, a result of the seminal "narrow interphase approximation" proposed by Helfand and Tagami. The composition profiles of the endblocks in these three blend cases indicate the absence of microphase separation (PU), micelles residing in the copolymer phase (PM) and cylinders oriented with their long axis parallel to the interface (PC||), respectively. Specific cases of repulsion parameter combinations are considered further below.

4.4.1.1 Case I: $\alpha_{AB} = \alpha_{BH}$

In this series, the B midblock possesses the same degree of incompatibility with hB as it does with the A endblocks. As summarized in the first row of ($\alpha_{AB} = 30$), the copolymer does not undergo microphase separation due to its relatively low interblock incompatibility, but the
blend macrophase-separates into dispersed domains of copolymer and homopolymer. At higher values of $\alpha_{AB}$ (= 60), the copolymer molecules form micelles at low $\alpha_{AH}$, but ultimately transform into perpendicular-oriented cylinders when $\alpha_{AH}$ is progressively increased to its highest value (= 90). Increasing $\alpha_{AB}$ at constant $\alpha_{AH}$ likewise generates transitions in copolymer morphology, as reflected in the composition profiles displayed in Figures 3a and 3b for the 70/60/60 and 70/90/90 systems. Similarly, discrete macroscale dispersions give way to planar blend morphologies as $\alpha_{AH}$ is systematically increased at constant $\alpha_{AB}$ (for $\alpha_{AB} \geq 60$) or as $\alpha_{AB}$ is increased at constant $\alpha_{AH}$. When $\alpha_{AB} = \alpha_{BH} = 90$ and all the blocks and homopolymer are highly repulsive, the blend morphology is consistently planar and the copolymer morphology remains cylindrical, with the cylinders eventually switching their orientation relative to the interface from perpendicular to parallel when $\alpha_{AH}$ is boosted to 90. In a somewhat related observation, Russell and co-workers\textsuperscript{70} have previously reported changes in cylinder orientation for molecularly-thin block copolymer films varying in thickness due to surface effects. Although the present result keeps the copolymer macrophase thickness constant, penetrable homopolymer surfaces nonetheless confine the copolymer macrophase. While it would be experimentally difficult to tune the value of $\alpha_{AH}$ through the use of different chemical species, $\alpha_{AH}$ can be alternatively controlled by varying the temperature (since $\alpha_{AH} \sim \chi_{AH}$ and $\chi_{AH} \sim 1/T$). The morphological features listed in Table 5, including cylindrical switching, are therefore amenable to experimental verification by using blends wherein the temperature can be reduced over a broad range.
4.4.1.2 Case II: $\alpha_{AB} < \alpha_{BH}$

In this series, the B midblock prefers to interact with the A endblocks than with homopolymer molecules, which would be tend to be undesirable in a real-world ABA/hB blend unless the copolymer is intended to serve, for instance, as a rubber-toughening "filler" in a brittle thermoplastic matrix. As in Case I above, copolymer molecules in blends with $\alpha_{AB} = 30$ remain unsegregated at all levels of $\alpha_{AH}$ and $\alpha_{BH}$, although an increase in $\alpha_{AH}$ systematically promotes a transition from D to P macrophase morphologies. When $\alpha_{AB}$ is increased to 60 (and $\alpha_{BH}$ is forced to equal 90 to preserve the condition of this case), however, the block copolymer self-organizes into spheroidal micelles. While we have not assigned an orientation for the micelles, it is important to recognize that the micellar lattice, when it develops, lies parallel (not oblique) to the polymer-polymer interface. This is evident from the composition profiles for the 70/30/60 (DU, Figure 3c) and 70/60/90 (PM, Figure 3d) systems in Figure 3. Even in cases of dispersed macrophase morphologies, the micellar unit cell, if present, is always observed to lie parallel to the local interfacial contour. Taken together, these results indicate that, if a block copolymer is intended solely for use as a filler, the blocks must be sufficiently incompatible to induce self-assembly into micelles or the copolymer will remain mixed within the homopolymer matrix. If the micelles are sufficiently incompatible to order on a lattice, the lattice will orient parallel to the polymer-polymer interface in close proximity to the interface, which, of course, will result in lattice defects far from the interface. It immediately follows that the extent of macrophase separation (D versus P) strongly influences the degree to which self-assembled copolymer molecules can exhibit long-range order.
4.4.1.3 Case III: $\alpha_{AB} > \alpha_{BH}$

In this last series, the homopolymer is midblock-selective, and the magnitude of $\alpha_{BH}$ is anticipated to play a significant role on the development of block copolymer morphology as it dictates the affinity of the B block for the homopolymer and, thus, the equilibrium concentration of homopolymer within the copolymer macrophase. As demonstrated both experimentally\textsuperscript{23} and theoretically\textsuperscript{25,32} this effect is strongly coupled with chain length, but chain length is not varied in the present study. According to the morphologies listed in Table 5, $\alpha_{AB}$ at constant or variable $\alpha_{BH}$ appears primarily responsible for the transition from block copolymer micelles to cylinders, which is not altogether surprising. An intriguing aspect of these results is that the interplay between $\alpha_{AH}$ and $\alpha_{BH}$ induces an orientation transition from perpendicular cylinders to parallel cylinders, with large values of both $\alpha_{AH}$ and $\alpha_{BH}$ favoring the latter. Note that the parallel cylinder orientation only occurs in P macrophase morphologies. When the homopolymer is highly B-selective ($\alpha_{BH} = 30$), it is more readily incorporated into the copolymer macrophase. As a consequence, the copolymer macrophase swells and thus occupies greater volume, which explains why most of the macroscopic morphologies encountered appear dispersed. In fact, the P morphology is only observed when the homopolymer is marginally midblock-selective at $\alpha_{BH} = 60$. These results establish that dispersed blend morphologies are readily achieved with a highly B-selective homopolymer and that the morphology of the copolymer macrophase is governed for the most part by the inherent incompatibility of the copolymer molecule (at constant chain length).
4.4.1.4 Blend Characteristics

Fitting the hyperbolic tangent function to the interfacial composition profiles generated from macrophase-separated ABA/hB blends exhibiting a planar morphology, followed by the procedure described in Section 2.2 with application of Eq. 3, yields values of the interfacial thickness ($\lambda$) between the copolymer and homopolymer macrophases. Values of $m$ extracted in the process from this analysis are found to range from 0.90 at lower segregation strength (broader interfaces) to 1.75 at higher segregation strength (narrow interfaces). The dependence of $\lambda$ on $\alpha_{AH}$ at two different $\alpha_{BH}$ for the specific cases of $\alpha_{AB} = 30, 60$ and $90$ is shown in Figure 4.

Several important features and trends warrant discussion. The first is that the magnitude of $\lambda$ agrees reasonably well with various experimental observations reported for polymeric systems in the literature.\textsuperscript{72–75} Secondly, as the homopolymer becomes increasingly midblock selective (lower $\alpha_{BH}$), $\lambda$ generally widens (by as much as $\approx 1$ nm), which can be attributed to a greater concentration of hB within the copolymer and, hence, a lower effective incompatibility between the copolymer and homopolymer macrophases. According to the Helfand-Tagami theory,\textsuperscript{69} $\lambda \sim \chi^{-1/2}$ at conditions of strong segregation. It immediately follows that, if the net incompatibility between the copolymer and homopolymer decreases due to a dilution effect, then $\lambda$ is qualitatively expected to increase, which is seen to be the case in Figure 4. As $\alpha_{AB}$ is increased (and the blocks comprising the copolymer become increasingly incompatible) from Figure 4a to Figure 4c, the magnitude of $\lambda$ tends to decrease, which can likewise be explained in terms of polymer-polymer interactions. The results presented in Figure 4 also reveal that an increase in $\alpha_{AH}$ initially promotes a monotonic reduction in $\lambda$, followed by a plateau where $\lambda$ is independent of $\alpha_{AH}$. While the onset of the plateau is generally insensitive to $\alpha_{BH}$, it appears to occur at lower
$\alpha_{AH}$ as $\alpha_{AB}$ is increased. The existence of a plateau is consistent with the development of a strong-segregation limit, and it is comforting to recognize that all the simulations yield values of $\lambda$ between ca. 5 and 6 nm in this limit.

In addition to the blend and copolymer morphologies and the interfacial thickness measurements, the simulations performed in this study provide valuable information regarding the network formed by the copolymer molecules and, by inference, the mechanical properties of the blend. In the same format as Figure 4, Figure 5 displays the copolymer bridging fraction ($f_B$) as a function of $\alpha_{AH}$ for different levels of $\alpha_{BH}$ at three different values of $\alpha_{AB}$. Upon cursory examination, these simulation results establish a valuable relationship, namely, $f_B$ is independent of $\alpha_{AH}$ and $\alpha_{BH}$ at low copolymer incompatibility (Figure 5a, where $f_B \approx 0$ because most of the chains are unsegregated and no network forms), as well as at high copolymer incompatibility (Figure 5c, where $f_B$ reaches a maximum level at 0.53 ± 0.02). It is important to recognize that, without any added hB, $f_B \approx 0.62$ in a comparable ABA copolymer melt under similar simulation conditions. At an intermediate copolymer incompatibility ($\alpha_{AB} = 60$ in Figure 5b), increasing either $\alpha_{AH}$ or $\alpha_{BH}$ yields larger values of $f_B$ up to the limit identified in Figure 5c. The reason why the lowest $f_B$ coincides with the lowest value of $\alpha_{BH}$ can be traced back to hB-induced copolymer swelling, which promotes an increase in the intermicrodomain distance (and a corresponding decrease in the probability that a midblock can span the distance and connect neighboring microdomains). Conversely, if hB is not very midblock-selective ($\alpha_{BH} = 90$ in Figure 5b), then the copolymer does not absorb much homopolymer and $f_B$ becomes independent of $\alpha_{AH}$. The results included in Figure 5 indicate that macrophase-separated ABA/hB blends with the most fully formed networks and expectedly best mechanical properties require a strongly-segregated
copolymers and a midblock-compatible homopolymer that does not swell the copolymer very much (which is most easily achieved by increasing the hB chain length).

4.4.2 Results from the Experimental Equivalent

In the previous section, the morphological and network characteristics of model macrophase-separated ABA/hB blends have been examined over a broad range of $\alpha_{AH}$, $\alpha_{AB}$ and $\alpha_{BH}$ values. From the simulations, we have elected to quantitate system parameters such as the interfacial thickness and midblock bridging fraction to identify the most important repulsion parameters and relate them back to blend morphology. The implications deduced from the trends observed in Figures 4 and 5 immediately provide insight into real-world experimental systems, neglecting the effect of chain length. In this section, the pairwise repulsion parameters listed in Table 2 are employed in simulations specifically designed to map the copolymer network (in terms of the midblock conformational fractions $f_B$, $f_L$, $f_D$, and $f_U$) as a function of distance from the polymer-polymer interface. On the basis of the repulsion parameters generated from solubility parameters in conjunction with Eqs. 1 and 2, it stands to reason that PE is strongly midblock-selective with $\alpha_{BH} \approx 25.4$ (recall that the lowest value of $\alpha_{BH}$ chosen in the preceding section was 30). In addition, the value of $\alpha_{AH}$ for SEBS/PE blends ($\approx 42.9$) is also below the minimum investigated in the previous section. Assuming a locally flat interface (which is ensured with melt-spun bicomponent fibers measuring as small as 30 µm in diameter), extrapolation of the trends evident in Figure 4 suggests that the interface of a PE/SEBS blend (with the repulsion parameter set 42.9/48.3/25.4) measures about 11-12 nm thick. To quantify the network characteristics
along the SEBS/PE interface and explain the basis for both interfacial adhesion and shape memory, we have performed a series of simulations according to the procedure described in Section 2.1.

Blends varying in composition from pure SEBS to pure PE are intended to replicate different slices along the interfacial composition profile fraction generated from simulations of the macrophase-separated SEBS/PE blend. That is, each composition along the profile is treated as a macroscopically homogeneous blend by simulating a small sample volume that is incapable of macrophase-separating. While the actual, macrophase-separated blend is 50 vol% SEBS, profile blends varying from 0 to 90 vol% SEBS are examined to determine the midblock conformational fractions. As expected from the trends in the previous section of this study, these variable-composition simulations yield blend morphologies that exhibit microphase separation of the SEBS copolymer. The density-based clustering algorithm DBSCAN is employed to identify the periphery of the copolymer micelles and permit direct measurement of $f_B$, $f_L$, $f_D$, and $f_U$. Pictured in Figure 6 are examples of the micellar morphology that develops in SEBS/PE blends at two different PE concentrations. Also included in Figure 6 are matching spatial diagrams indicating the distributions of dangling ends and unsegregated copolymer molecules, since they serve as noise by not fully contributing to micelle development (i.e., by forming either bridges or loops). Results extracted from these two example blend compositions are mapped onto the interfacial composition profile of the macrophase-separated blend, which is provided in Figure 7a. Midblock conformational fractions measured at different PE concentrations along the profile are presented as a function of distance along the interfacial normal in Figure 7b. As the
profile is traversed from SEBS-rich to PE-rich (left to right), $f_B$ and $f_L$ both decrease due to a reduction in the population of SEBS molecules and the corresponding PE-induced increase in intermicrodomain distance due to swelling. The fraction of chains existing as dangling ends, $f_D$ increase linearly up to 70% PE by volume. Beyond 70% PE $f_D$ diminishes rapidly to 0.1 at 90% PE composition. Lastly, unsegregated fraction of chains with both endlocks in the EB phase $f_U$ is insignificant (< 0.05) up to 50% PE composition. Beyond 50% PE the unsegregated fraction of chains grows considerably to 0.86 at 90% PE volume. Complementary attempts to extract these fractions directly from volumetric slices of the simulated macrophase-separated polymer blend (for quantitative comparison with the results given in Figure 7b) significantly undercount chain populations due to finite volume effects.

Analogously the molecular network formation in PP/SEBS interfacial systems is described in Figure 8. Due to an increased incompatibility between the PP homopolymer and the styrenic endblock beads (refer Table 2) compared to that of PE, the SEBS chains prefer to exist as bridges or loops as opposed to dangling and unsegregated chains. The values of $f_B$ are therefore about 3-5% higher compared to that of PE/SEBS system on the SEBS rich side of the interface. As the PP volume fraction increases beyond 0.4, $f_L$ increases to about 42% surpassing $f_D$. Such a contrast with PE/SEBS is expected due to the fact that the S-PP incompatibility is significantly higher than endblock-PE incompatibility whereas the EB-PP and EB-PE incompatibilities are similar. Hence, looping of endblocks is more energetically favorable than dangling end conformations. Another supporting evidence of this conjecture is the low $f_U$ (< 5% even at 0.5 PP volume fractions) in the PP/SEBS system.
4.5. Conclusions

We have investigated the interfacial morphologies in triblock copolymer (ABA)/homopolymer (H) systems with a wide range of $\alpha_{AH}$, $\alpha_{AB}$, and $\alpha_{BH}$ repulsion parameters using DPD simulations. The copolymer and homopolymer components exhibit macrophase segregation only if $\alpha_{AH} > 50$ and $\alpha_{BH} > 50$ else the copolymer was observed to be dispersed in the homopolymer component. Within the triblock copolymer component, we have noticed the self-assembly of micelles for $\alpha_{AB} = 60$, and hexagonally packed cylinders for $\alpha_{AB} = 90$. The microdomain lattice direction in the copolymer component is preferentially perpendicular to the copolymer/homopolymer interface if $\alpha_{AH} < 70$ as evidenced by the density profile measurements. For $\alpha_{AH} > 70$ the cylindrical domains orient themselves parallel to the interface. No microphase segregation was noted for $\alpha_{AB} = 30$. The interfacial thickness has been estimated to be in the range 5 -6 nm for strong segregation $\alpha_{AH} > 70$, and 12-14 nm for moderately segregating regimes $\alpha_{AH} < 60$. The interfacial thickness decreases linearly with $\alpha_{AH}$ up to $\alpha_{AH} = 70$ and levels off. Increasing midblock/homopolymer repulsion ($\alpha_{BH}$) also caused the interfacial thickness to diminish faster with $\alpha_{AH}$. For the systems mimicking physically studied materials, we have studied the bridging and looping fractions as a function of the blend composition and predict that this trend is valid in compositional space along the interface between the polyethylene and styrene-co-(ethylene-butylene)-co-styrene (SEBS) system. The bridging fraction decreased linearly with the increase of midblock affinitive PE content in the SEBS matrix. When mapped on to the interfacial density profile, this indicates a decrease according to the hyperbolic tangent profile along the interfacial distance. A corresponding increase in the dangling ends is noticed up to 70% PE
volume content above which there is a sharp decrease to 0.05 at 90% PE. The looping fraction in the SEBS copolymer remained around 0.25 up to 70% PE and dropped linearly with PE content beyond 70%. An insignificant fraction (< 0.05) of chains exist as unsegregated molecules up to 50% PE and following that there is a sudden increase to $f_U = 0.86$ at 90% PE volume content. For PP/SEBS system the SEBS chains preferentially exist as bridges and loops as compared to dangling ends. Overall bridging fractions in PP/SEBS system were observed to be 3-5% higher than in PE/SEBS. Whereas the looping fraction, about 40-42%, exceeded dangling end chain fraction (25-30%) on the PP rich half of the interface.

4.6. Acknowledgments

This study was supported by the Nonwovens Cooperative Research Center at North Carolina State University, grant number 10-127. The authors would like to thank David Williams and Kenneth Mineart for their help in running some of the simulation runs.
4.7. References


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(65) Tallury, S. S.; Pasquinelli, M. A.; Pourdeyhimi, B.; Spontak, R. J. *In Preparation 2013*.


Table 4.1. The pair repulsion parameters employed in the systematic study. All of these values are expressed in DPD energy units ($k_B T = 1.0$ at $T = 373$ K). In the text, the simulation set being discussed is identified as $\alpha_{AH} - \alpha_{AB} - \alpha_{BH}$.

<table>
<thead>
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<th>$\alpha_{BH}$</th>
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<th>$\alpha_{AH} = \alpha_{AB}$</th>
<th>when $\alpha_{AH} &gt; \alpha_{AB}$</th>
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Table 4.2. Pair repulsion parameters for the species included in simulating the experimental equivalents.

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<th>PE</th>
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<th>EB</th>
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<tr>
<td>S</td>
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<tr>
<td>EB</td>
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Table 4.3. The different microphase morphologies and orientations predicted from the DPD simulations when the macrophase morphology is classified as “Dispersed”.

<table>
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<tr>
<th>Symbol</th>
<th>D U</th>
<th>D M</th>
<th>D C</th>
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</thead>
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<tr>
<td>Microphase Morphology</td>
<td>Unsegregated</td>
<td>Spherical Micelles</td>
<td>HCP Cylinders; parallel to macro-interface</td>
</tr>
<tr>
<td>DPD Snapshot</td>
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<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td>Specific System</td>
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<td>50/60/30</td>
<td>50/90/30</td>
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</table>
Table 4.4. Same as Table 4.3, but for when the macrophase morphology is classified as “Planar” and thus there is a distinct, flat interface between the homopolymer and copolymer systems, so the density profile relative to that interface of each component can also be calculated; the legend for the density profile plots is similar to 60/30/30 in all cases. Also note that the microphase morphology can be classified as being parallel (∥) or perpendicular (⊥) to the macro-interface.

<table>
<thead>
<tr>
<th>Microphase Morphology</th>
<th>Unsegregated</th>
<th>Micelles; lattice plane parallel to macro-interface</th>
<th>Cylinders; lattice plane parallel to macro-interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
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<td>P M∥</td>
<td>S C∥</td>
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<td>90/90/90</td>
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Table 4.5. Summary of types of phase morphologies from Tables 3 and 4 that were observed for each system in Table 1; the snapshots for the systems not given Tables 3 and 4 are given in the Appendix. The key is as follows: The first letter indicates the macrophase behavior, either dispersed (D) or planar (P); The second letter indicates the microphase behavior, either unsegregated (U), body-centered cubic micelles (M), or hexagonally-packed cylinders (C). Also indicated is whether the microphase features are parallel (||) or perpendicular (⊥) to the macro-interface.

<table>
<thead>
<tr>
<th>$\alpha_{AB}$</th>
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Figure 4.1. A schematic of the homopolymer (green) and ABA triblock copolymer (red/blue) system. The various types of pair repulsion parameters are also indicated between the endblocks and the homopolymer ($\alpha_{AH}$), between the midblock and the homopolymer ($\alpha_{BH}$), and between the endblock and midblock beads in the copolymer ($\alpha_{AB}$).
Figure 4.2. Predicted homopolymer/copolymer interfacial density profiles for the simulations showing macrophase segregation (cf. Table 4). The repulsion parameters for the three examples are are (a) 60/30/30, (b) 50/90/90, and (c) 90/90/90. Representations are similar to a) throughout.
Figure 4.3. The predicted homopolymer/copolymer interfacial thickness values as a function of $\alpha_{AH}$ for (a) $\alpha_{AB} = 30$, (b) $\alpha_{AB} = 60$, and (c) $\alpha_{AB} = 90$. 
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Figure 4.5. Network formation as a function of $\alpha_{AH}$ for (a) $\alpha_{AB} = 30$, (b) $\alpha_{AB} = 60$, and (c) $\alpha_{AB} = 90$. 

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**a)**

**b)**

**c)**

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Chapter 5

Shape-Memory Behavior of Melt-Spun Bicomponent Filaments with Variable Interfacial Area

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Abstract

Melt spun bicomponent filaments composed of a poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) core and a linear low-density polyethylene (LLDPE) sheath have recently been shown to exhibit excellent thermally-activated shape-memory. To ascertain the role of the core-sheath interface, we have examined the morphology and mechanical property attributes of bicomponent filaments measuring 82 μm across and composed of multiple SEBS sub-filaments discretely arranged in a continuous LLDPE matrix (the so-called "islands-in-the-sea" design) in which interfacial area increases with the number of islands (Ni). Filaments prepared with four different values of Ni – 1, 12, 37 and 61 – have been generated at a composition of 50 vol% SEBS, and their shape fixity and recovery ratios have been measured in uniaxial tension. Both ratios tend to decrease with increasing Ni due presumably to the increasing frailty of the SEBS sub-filaments, which measure as thin as 40 μm in diameter when Ni = 61. By systematically investigating the effect of composition on the shape-memory behavior of bicomponent filaments with 61 islands, we find that the most promising shape memory performance is achieved with filaments containing between 60 and

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80 vol% SEBS. At lower SEBS concentrations, plastic deformation of the LLDPE matrix compromises shape memory, especially after cycling.

5.1. Introduction

Shape-memory polymers (SMPs) preserve one or more temporarily programmed deformed states until an external stimulus "triggers" the materials to return close to their original shape.\textsuperscript{1,2} While SMPs can be designed to respond to many different stimuli, thermally-activated shape-memory remains the most common response mechanism.\textsuperscript{3–5} The popularity of thermal activation can be attributed to not only the ease of applying SMPs to a particular end-use application, but also the variety of several chemical and physical phenomena from which to choose in devising a shape-memory polymer network.\textsuperscript{4} Numerous studies have focused on SMPs generated from chemically cross-linked species in conjunction with either a thermally-responsive segment in the backbone or a triggering species confined within the network.\textsuperscript{6} The channels comprising interpenetrating networks (IPNs) can likewise be designed to respond to different temperatures, thereby creating the possibility to program more than one temporary shape in the network.\textsuperscript{7,8}

While a custom-synthesized chemical network provides versatility in the design of preparing new SMPs, significant shortcomings and limitations accompany this traditional approach.\textsuperscript{9} Eventual environment-, time- or application-induced embrittlement of the chemically cross-linked network, limitations in repetitive mechanical cycling even at low strains, poor scalability due to the stochastic nature of chemical cross-linking, and high costs associated with large-scale production constitute significant drawbacks to the conventional manufacture of SMPs and thus negatively impact the widespread use of most contemporary
SMPs. Moreover, once a chemically cross-linked network is set, the material cannot be easily reprocessed, thereby hindering the reuse and recycling of such materials. Molecular network formed by physical means, on the other hand, are dictated by thermodynamics, which tend to be more robust and predictable. It is a common practice in engineering plastics to incorporate thermodynamically incompatible segments of polymers along a polymer backbone to achieve phase segregation at nanoscopic length scales, as exemplified by block copolymers. Although the chemical route required to prepare such molecules is sometimes nontrivial, advances in the chemical synthesis of copolymers have succeeded in allowing these materials to become ubiquitous in numerous and diverse technologies.

Physical networks in SMPs have been generated in segmented polyurethanes, as well as randomly-coupled multiblock copolymers composed of poly(ethylene terephthalate), polyamide or polynorborne moieties, to name a few.

A facile physical strategy of SMP materials that permit commercial-scale manufacture and provide widespread use is still needed. The present work focuses on designing a process, rather than chemical, means of achieving thermally-activated shape memory without involving custom molecular synthesis or chemical cross-linking. Considerable effort has been invested in the development of manufacturing techniques that facilitate commercial-scale production of thermoplastics, including SMP materials. Melt-spinning, for instance, is an established method to generate high-aspect-ratio filaments at a very high production rate. We have previously demonstrated the use of bicomponent melt-spinning to thermally weld a commercially available thermoplastic elastomer, namely, poly[styrene-\textit{b-}\textit{(ethylene-co-butylene)-b-styrene}] (SEBS), and a block-compatible homopolymer, linear low-
density polyethylene (LLDPE), to prepare thermally versatile SMPs. Here, we examine the
effect of filament cross-sectional geometry (and, thus, interfacial area) on the shape-memory
behavior of SEBS/LLDPE bicomponent filaments.

Early studies of bicomponent melt-spinning\textsuperscript{20-22} are responsible for the development of
the so-called "islands-in-sea" cross-sectional geometry. Filaments possessing this
morphology consist of multiple sub-filaments of one species (islands) embedded in a
continuous matrix of another (sea) along the filament axis. Such filaments have been used to
yield high-strength nylon webs\textsuperscript{23} and to prepare high-surface-area substrates for filtration.\textsuperscript{24,25}
The adjustable nature of this process uniquely allows for control over interfacial area and,
hence, property evolution with different numbers of islands in the sea ($N_I$), as well as
different compositions.\textsuperscript{26} The latter effect has been recently investigated in melt-pressed
blends (not filaments) composed of a poly(styrene-$b$-butadiene-$b$-styrene) (SBS) triblock
copolymer and poly($\varepsilon$-caprolactone) (PCL) and exhibiting shape memory.\textsuperscript{27} Our objective in
the present study is to discern, from both morphological and property viewpoints, the
coupled effects of interfacial area and composition on the shape-memory behavior of
bicomponent SEBS/LLDPE filaments.

5.2. Materials

The SEBS triblock copolymer (SEBS) used in this study was kindly obtained from
Kraton Polymers Inc. (Houston, TX). According to the manufacturer, the molecular weight
and composition of this copolymer grade (G1643), which is suitable for melt-spinning, were
20 wt\% S, respectively. The LLDPE (Engage 8402), provided by the Dow Chemical Co.
(Midland, MI), was a poly(ethylene-co-octene) copolymer developed primarily for injection molding. It was melt-spun into filaments here using lower spinning speeds and draw-down ratios than those commonly employed in conventional melt-spinning operations, as detailed below. The composition of the filaments in which N was systematically varied was held constant at 50 vol% SEBS, whereas the composition was varied from 20 to 80 vol% SEBS in 10 vol% increments in filaments with N = 61. Due to the relatively high process temperatures encountered during melt spinning, 3 wt% Irganox 1010 (BASF corporation) was added as a stabilizing agent. To ensure that the filament compositions reported here are accurate, the extruders and spinnerets were thoroughly cleaned prior to each run.

5.3. Experimental Methods

5.3.1 Production of Bicomponent Filaments

Filaments featuring islands-in-the-sea cross-sections were produced on a bicomponent melt-spinning apparatus manufactured by Hills Inc. (Melbourne, FL) and equipped with three different spin packs yielding 12, 37 and 61 islands. The temperature profiles (listed in Table 1), spinning speed (250 m/min) and zero draw-down ratio maintained during melt spinning yielded filaments varying in N and/or composition that consistently measure between 75 and 100 μm in diameter (the variation within a given run is estimated as ± 7%). Filaments were collected about 1 m below the quenching zone by winding directly onto a spool.
Table 5.1. Melt-spinning conditions employed for bicomponent SEBS/LLDPE filaments.

<table>
<thead>
<tr>
<th></th>
<th>Pressure (MPa)</th>
<th>Extruder Temperature (°C)</th>
<th>Quenching Air Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zone 1</td>
<td>Zone 2</td>
</tr>
<tr>
<td>SEBS (Extruder A)</td>
<td>5.2</td>
<td>210</td>
<td>220</td>
</tr>
<tr>
<td>LLDPE (Extruder B)</td>
<td>11.4</td>
<td>190</td>
<td>195</td>
</tr>
</tbody>
</table>

5.3.2 Characterization of Bicomponent Filaments

Optical images of filament cross-sections were acquired using a Nikon Eclipse 50i POL microscope, whereas scanning electron microscopy (SEM) was performed on cross-sectioned filaments with a FEI Quanta 3D field-emission instrument. To obtain representative cross-sections and emphasize the SEBS sub-filaments, the filaments were cryofractured under liquid nitrogen and, in limited cases, bent to expose the sub-filaments prior to specimen attachment and subsequent imaging. In addition, the discrete islands residing in LLDPE were highlighted by exposing the filaments to liquid toluene for 12 h under quiescent conditions, followed by vacuum-drying for 2 h, to selectively dissolve the copolymer and leave behind holes. Metal sputter coating was not applied on the filaments to preserve delicate morphological features by avoiding thermal damage or masking. The thermal characteristics of the filaments were investigated by differential scanning calorimetry (DSC) performed on a Perkin-Elmer Diamond calorimeter. Thrice-replicated samples were subjected to a heating rate of 10°C/min from 25 to 200°C so that the upper glass transition temperature ($T_g$) of the styrenic copolymer and the melting temperature ($T_m$) of the LLDPE filament matrix could be identified in filaments differing in N and/or composition. From
these tests, $T_g \approx 93 \pm 4 ^\circ C$ and $T_m \approx 65 \pm 3 ^\circ C$ irrespective of morphology and SEBS content.

Thermal shape-memory analysis of the filaments was performed by dynamic mechanical analysis (DMA) on TA Instruments Rheometrics Solids Analyzer III. Specimens were prepared from bundles of 80-100 filaments selected to maintain a constant cross-sectional area. Tests conducted at gauge lengths ranging from 5 to 50 mm revealed that a gauge length of 10 mm was suitable for reproducibility. Evaluating the shape-memory performance involved the measurement of strain stored in a temporary state, as well as the recovered strain after thermal treatment. The shape-memory testing procedure followed the sequence of events listed below:

a) Start the test at a gauge length of 10 mm and then heat the sample to 75ºC (which is above $T_m$ of the LLDPE sheath but below the upper $T_g$ of the SEBS core).

b) Increase the uniaxial tensile load at a constant strain rate of 0.01 s$^{-1}$ to a target strain level (between 70 and 170%).

c) Hold the specimen at the prescribed strain for 5 min and then rapidly cool to 30 ºC to lock-in (program) the temporary strain state.

d) Remove the load and measure the strain at a very small tensile load (~ 0.1 Pa) to emulate stress release.

e) Reheat the specimen to 75ºC to permit strain relaxation and measure the irreversible strain upon recovery.

f) Repeat each of the steps above for successive shape-memory cycling.
5.4. Results and Discussion

5.4.1 Morphological Analysis

Since the properties of bi/multicomponent fibers are intimately tied to their internal morphology, we have employed optical and scanning electron microscopy to evaluate the cross-section of bicomponent filaments containing different values of $N_I$ (i.e., the number of SEBS sub-filaments, or islands) and/or different SEBS concentrations. In Figure 1a, a longitudinal schematic depicting an islands-in-the-sea filament is presented, whereas cross-sectional scanning electron micrographs acquired from two different series of filaments generated here are provided in Figure 1b. The first series is designed to hold the concentration of SEBS constant at 50 vol% and vary $N_I$ from 12 to 61 to deduce the effect of increasing the SEBS/LLDPE interfacial area with increasing $N$ on shape-memory attributes. If the average filament diameter remains constant (82 ± 5 μm in Figure 1b) during melt-spinning and across a series of specimens, then volume conservation along the full length of a filament can be equivalently treated as area conservation along the filament cross-section.

Assuming a 1:1 SEBS/LLDPE volume ratio and comparable mass densities, the condition of equal area requires that $N_I \pi r^2 = \pi (R^2 - N_I r^2)$, where $r$ and $R$ denote the radii of the sub-filaments (islands) and bicomponent filament, respectively. From this area balance (which yields $r = R/\sqrt{2N_I}$) and recognizing that the interfacial area ($A$) is given by $2N_I \pi r$, $A$ can be conveniently written in terms of design parameters as

$$A = (\sqrt{2N_I}) \pi R$$  \hspace{1cm} (1)

In the second series of filaments portrayed in Figure 1b, the number of islands is maintained at 61 and the SEBS concentration is systematically varied from 20 to 80 vol% SEBS in 10...
vol% increments. As above, $A$ can also be directly related to the volume-fraction concentration of SEBS ($\phi$) through a comparable area balance, which results in

$$A = 2\pi R \sqrt{\phi N_I} \tag{2}$$

When $\phi = 0.5$ in the case of the first filament series with variable $N_I$, Eq. 2 reduces to Eq. 1.

Corresponding higher magnification SEM images showing representative cross-sections of bicomponent filaments with 50 vol% SEBS are provided in Figure 2. In Figure 2a, the SEBS sub-filaments in a filament with $N_I = 12$ were forced to protrude from the surface by bending the filaments after cross-fracturing. Note that, because of their compliant nature, the SEBS sub-filaments do not retain circular cross-sections but instead adopt a distorted cardioid shape. Alternatively, upon dissolution of SEBS in toluene, the remaining filament with $N_I = 37$ only displays the LLDPE (sea) matrix (cf. the SEM image in Figure 2b). The resulting holes in images such as the one provided in Figure 2b measure 16.5 $\mu$m in diameter on average. Images of filaments with $N_I = 37$ after removal of the SEBS sub-filaments are compared along the fiber axis and in cross-section in Figures 2c and 2d, respectively. While the longitudinal view in Figure 2c reveals the formation of striations on the filament surface when the sub-filaments reside in close proximity to the surface, the cross-sectional view in Figure 2d indicates that these sub-filaments near the filament surface occasionally rupture. For filaments with $N_I = 61$ we conclude that the interfacial area between SEBS and LLDPE scales geometrically as $\sqrt{N_I}$ in accordance with Eqs. 1 (constant $\phi = 0.5$, variable $N_I$) and 2 (variable $\phi$, constant $N_I = 61$).
5.4.2 Shape-memory behavior

The thermally-activated shape-memory behavior of the bicomponent filaments generated here has been interrogated by testing the mechanical properties of bundles of filaments at three different strain states. For illustrative purposes, we consider first the results provided in Figure 3, which displays the time evolution of stress and strain levels, as well as temperature, during the analysis of SEBS/LLDPE filaments with \( N_I = 12 \). The test starts at 70°C to soften the LLDPE matrix and endow the LLDPE molecules with sufficient mobility to deform as a liquid. According to complementary DSC measurements, \( T_m \) for the grade of LLDPE employed here is about 65°C. The choice of starting temperature likewise reflects the network stability of the SEBS islands, since the upper \( T_g \) of the SEBS copolymer is measured to be 93°C (which means that the styrenic micelles responsible for network formation remain intact at 70°C). After thermal equilibration, a strain of 170% is introduced during the first 100 s of the test. During this isostrain condition, the specimen starts to undergo stress relaxation. After this initial part of the test, the temperature is ramped down to 30°C, thereby fixing the strain-state in the filaments due to recrystallization of the LLDPE matrix. Once the temperature equilibrates after about 400 s, stress relaxation appears to stabilize at a final stress of 4.8 MPa.

When the applied load is released at 600 s, the instrument tries to keep the sample taut while keeping the filaments in very low tension from 600 to 900 s. During this time interval, the stress and strain levels exhibit a dampened oscillatory response, which we extrapolate to about 150% strain at infinite time by applying a hyperbolic function to the data. When the instrument oscillates above a particular strain, a corresponding stress registers, indicating that
the filaments are engaged. The strain at which the instrument reaches a plateau from 600 to 900 s is the temporary strain state fixed in the LLDPE matrix. The corresponding strain fixity ratio \( S_f \) is determined from

\[
S_f = \frac{Unrecovered\ strain}{Maximum\ strain} \times 100\% \tag{3}
\]

From the results shown in Figure 3, we calculate \( S_f = 93.4 \pm 4.1\% \). After 900 s, the temperature is increased back to 70ºC while maintaining slight tension to follow the material response. At this stage the LLDPE molecules are once again mobile, but the strained SEBS network recovers the deformation rapidly. Achieved in less than 2 s, the final recovered strain is consequently used to measure the strain recovery ratio \( S_r \) according to

\[
S_r = \frac{Recovered\ strain}{Maximum\ strain} \times 100\% \tag{4}
\]

Since the final strain state in Figure 3 is about 47%, the recovered strain is 123%, which translates into \( S_r = 72.3\% \). Thus, the strain fixity and recovery ratios of 93.4 and 72.3% characterize the shape-memory behavior of the SEBS/LLDPE filaments with \( N_f = 12 \) under programmed heating for a single cycle. This procedure is repeated for 5 successive cycles to investigate the mechanical response following initial shape memory.

Shape memory has been investigated at strain levels of 70, 120 and 170% to discern if the maximum strain influences fixity and recovery. In Figure 4, the DMA results measured from 60/40 v/v SEBS/LLDPE filaments with \( N_f = 61 \) are provided at 70% (Figure 4a) and 170% (Figure 4b). In general and as demonstrated in Figure 4, \( S_f \) tends to be higher when the maximum strain is set beyond 100%, whereas \( S_r \) exhibits no noticeable dependence on the maximum strain. For example, at 70% maximum strain in Figure 4a, \( S_f = 77.8\% \) and \( S_r = \)
85.4%. At 170% strain in Figure 4b, $S_f$ increases modestly to 91.1%, and the strain recovery remains nearly constant at 77.6%. At the intermediate maximum strain examined here (120%, data not shown), the fixity and recovery ratios are found to be 92.3 and 85.6%, respectively. These observations suggest that the strain recovery is dictated by the effectiveness of the SEBS network, which is, in turn, governed by the thermodynamics associated with microphase separation of the S and EB blocks. Unlike chemically cross-linked networks, the physically cross-linked network of the copolymer is attributed to the formation of bridged EB blocks that connect glassy S-rich micelles. Since melt spinning employs short residence times within the extruder, it would not be surprising if the copolymer network possessed a nontrivial population of defects, that is, non-bridged EB blocks that develop as loops or parts of dangling ends. The first shape-memory cycle is therefore anticipated to display evidence of hysteresis due to the existence of such network defects, which would translate into a constant recovered strain irrespective of the maximum strain utilized in the analysis. The fixity, on the other hand, is likely to reflect the organization of recrystallized LLDPE crystals. At 70% strain, the SEBS network is not as highly deformed as (and would try to recover more slowly and with less force than it would) if it were strained to 170%. It follows that the LLDPE crystals would lock into place at shorter times and at higher fixity levels in filaments subjected to higher maximum strain levels. For this reason, results reported hereafter correspond to DMA measurements evaluated at a maximum strain of 170%.

As mentioned earlier, the interfacial area ($A$) between the SEBS islands and LLDPE matrix at 50 vol% SEBS varies with $\sqrt{N_f}$ according to Equation 1 in the limit of isochoric
filaments in which volume is additive, which is reasonable for nonpolar polymeric species such as SEBS and LLDPE. To ascertain the dependence of the strain fixity and recovery ratios on interfacial area in terms of the strain fixity and strain recovery ratios, we have analyzed filaments differing in $N_I$ from 12 to 61, and the results are shown in Figure 5 in which $S_r$ and $S_f$ are plotted as function of $A$. Included in this figure are the strain ratios measured from core-shell SEBS/LLDPE bicomponent filaments, which serve as the limiting case with a single island. Here, the values of $R$ used to calculate $A$ at each $N_I$ correspond to the average of the filaments with that particular $N_I$. These results indicate that $S_f$ does not depend strongly on interfacial area, decreasing slightly with increasing $N_I$ beyond $N_I = 12$. In marked contrast, the strain recovery initially undergoes a significant reduction from 87.2 to 73.5% as $A$ is increased from $N_I = 1$ to $N_I = 12$ and then remains relatively constant (within experimental uncertainty) as $A$ is increased further. As mentioned earlier, the fixity reflects the extent to which the LLDPE crystals lock into place upon release of the applied load and is not expected a priori to be strongly sensitive to the SEBS network. According to DSC analysis, the crystallinity of these filaments does not change appreciably (from 10.2 to 11.5%) as $N_I$ (and $A$) is increased from 1 to 61, which is consistent with a relatively constant strain fixity ratio. The strain recovery, on the other hand, is a measure of SEBS network integrity. As the interfacial area is increased, the amount of LLDPE mixed into the SEBS sub-filaments increases, thereby swelling the copolymer and reducing the fraction of bridged midblocks that are responsible for network formation. In addition, the number density of network defects is also anticipated to become more pronounced as the sub-filaments decrease in size (as $N_I$ increases) due to increasing confinement effects. The results evident in Figure 5
provide insight into the molecular network and trigger responsible for shape memory in bicomponent filaments.

Similar trends are apparent from the results presented in Figure 6 for SEBS/LLDPE bicomponent filaments with 61 islands and variable composition after a single cycle. This particular morphology, for which $A \sim \sqrt{\phi}$, is selected since it is expected to suffer the most in terms of shape-memory degradation on the basis of the molecular-level descriptions introduced above. As in Figure 5, the strain fixity increases slightly but is not, in general, strongly affected by filament composition at LLDPE concentrations above 20 vol%, whereas the strain recovery likewise appears to be independent of LLDPE concentration (within experimental error). These observations are consistent with our proposed molecular model in which the strain fixity and recovery ratios are generally regulated by LLDPE crystal arrangement and SEBS network integrity, respectively. The recovery is found to correlate with the increase in the interfacial area as the SEBS network encloses more LLDPE with increased interfacial adhesion. As alluded to earlier, we postulate that, since melt spinning bicomponent filaments occurs rapidly under highly nonequilibrium conditions, the copolymer network is not afforded ample opportunity to develop to its fullest extent at thermodynamic equilibrium. To support this contention, the filaments varying in composition with 61 SEBS islands have been subjected to 5 consecutive shape-recovery cycles. The results of this mechanical cycling analysis are provided in Figure 7 and establish several intriguing trends, the most important of which is that the shape-memory attributes of these filaments (which are relatively unimpressive with respect to the core-shell baseline with $N_I = 1$) improve substantially in some cases with increasing cycle number (n).
In the case of the strain fixity, the results after the first cycle in Figure 8 range from 84.2 to 89.5%, whereas they increase noticeably to 91.5 – 93.4% and exhibit little dependence on filament composition after 5 cycles. These results confirm that the LLDPE becomes equally effective at locking-in a temporary strain state at low or high concentrations within the filaments, and that cyclic tensile loading assists in the molecular orientation of the crystals that form in the LLDPE. Note that, according to DSC analysis, cycling does not greatly affect the crystallinity of the LLDPE matrix (which ranges from 10 to 12%). The remarkable aspect of the data provided in Figure 8 is that the strain recovery increases dramatically upon shape-memory cycling at high SEBS concentrations. Consider the case with 80 vol% SEBS. The corresponding strain recovery ratio jumps from 78.2% after the first cycle to 92.1% after the fifth cycle, which is a consequence of network refinement due to repeated deformation. Similarly impressive results are observed when the SEBS concentration is decreased to 60 vol%. At lower SEBS concentrations from 40 to 60 vol%, however, less pronounced improvement in strain recovery due to shape-memory cycling is observed, whereas a precipitous drop in recovery occurs at SEBS concentrations below 40 vol%. Under these conditions, the shape and continuity of the SEBS sub-filaments fail and the materials undergo repeated plastic deformation. Therefore, although the bicomponent filaments possessing an islands-in-the-sea morphology do not generally perform as well as their core-shell analogs ($N_I = 1$) after single stimulation, we have established that mechanical cycling is capable of generating SMPs with comparable, if not superior, shape-memory attributes even in the most fragile of the filaments examined (with $N_I = 61$).
5.5. Conclusions

We have investigated the efficacy of thermally responsive shape-memory effect in filaments prepared by melt-spinning of SEBS and LLDPE with islands-in-sea cross-section. Firstly, we investigated filaments with different number of SEBS islands in LLDPE sea were produced at 1:1 volume ratio to study the effect of interfacial area on the shape-memory performance. Three different filaments i.e., with 12, 37, and 61 islands were compared including a limiting case of sheath/core bicomponent (1 island) from our previous work. We report inferior shape-fixity and shape-recovery ratios in the first cycle to that of the sheath/core cross section. In general the shape-fixity gradually decreases (by 5%) with the number of islands whereas the shape-recovery registers no particular trend. In a second series of experiments, filaments with 61 islands-in-sea at different SEBS/LLDPE volume ratio were subjected to shape-memory characterization for 5 consecutive cycles. The shape-fixity ratios remain fairly constant at 90-95% with the composition but increase by 5% over the shape-memory cycles. Shape-recovery response however was registered as diminishing beyond 50% LLDPE content in the filaments. This effect is magnified as the number of cycles increased. The best shape-memory behavior was noticed at 60/40 SEBS/LLDPE volume ratio with about 95% of shape-fixity and shape-recovery ratios.

5.6. Acknowledgments

This study was supported by the Nonwovens Cooperative Research Center at North Carolina State University. We thank Jerry Taylor and Tri Vu for technical assistance with regard to melt spinning, Hills Inc. for providing some of the spin packs and Dr. J. E. Flood for enlightening discussions.
5.7. References


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Figure 5.1. a) A schematic representation of the islands-in-sea filament; b) Scanning electron micrographs of the 50/50 SEBS/LLDPE islands-in-sea filament cross-sections for i) 12, ii) 37, iii) 61 islands; filaments with 61 islands and iv) 30/70, v) 50/50 and vi) 70/30 LLDPE/SEBS volume ratio respectively.
Figure 5.2. Scanning electron micrographs obtained for (a) SEBS component in 12 islands-in-sea, (b) LLDPE component in 37 islands-in-sea filaments. Figures (c) and (d) provide the lower magnification images of longitudinal and cross sectional views of LLDPE component in the 37 islands-in-sea filaments.
Figure 5.3. Shape-memory behavior of 50/50 SEBS/LLDPE filaments with 12 islands-in-sea cross-section. The solid line indicates the strain, dashed line indicates the stress and dotted line represents the temperature state of the filament sample.
Figure 5.4. Shape-memory behavior of 60/40 SEBS/LLDPE filaments with 61 islands-in-sea cross-section at 70% maximum strain. The curve representation is same as in Figure 3.
Figure 5.5. Shape-memory behavior of 60/40 SEBS/LLDPE filaments with 61 islands-in-sea cross-section at 170% maximum strain. The curve representation is same as in Figure 3.
Figure 5.6. Strain fixity and strain recovery ratios for SEBS/LLDPE filaments with different number of islands-in-sea as a function of interfacial area (the calculated interfacial area for a gauge length of 10 mm following the equation 3.).
Figure 5.7. Strain fixity and strain recovery ratios measured for SEBS/LLDPE filaments with 61 islands in sea at different SEBS/LLDPE volume ratios as a function of interfacial area (the calculated interfacial area for a gauge length of 10 mm following the equation 3.).
Figure 5.8. Evolution of strain fixity and strain recovery ratios with successive shape-memory cycles for 61 islands in sea SEBS/LLDPE filaments as a function of composition.
Chapter 6

Phase and Conformational Evolution of Molecularly Asymmetric Triblock Copolymers

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6.1 Abstract

Block copolymers remain one of the most extensively studied and ubiquitous classes of soft materials to date due to their unique abilities to form periodic nanostructures, alter interfacial thermodynamics and stabilize nanoscale laminates. Molecularly asymmetric triblock copolymers are progressively grown from a parent diblock copolymer and can elucidate the conformational transition from a single- to double-tethered midblock, which results in the formation of midblock bridges that are largely responsible for the production of elastic molecular networks that impart shape memory and bidisperse brushes that affect

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interfacial chain packing and, thus, morphology. Combining an arsenal of theoretical and simulation methods, we relate copolymer asymmetry to phase behavior and midblock conformations, which become highly temperature-dependent as the order-disorder transition is approached. Monte Carlo simulations yield a novel isothermal phase diagram that is explicitly expressed in terms of molecular asymmetry.

6.2 Introduction

Block copolymers remain one of the most extensively studied genres of macromolecules to date due to their innate ability to (i) self-organize spontaneously into a wide variety of periodic nanostructures\(^1,2\) and (ii) compatibilize immiscible polymers,\(^3,4\) as well as stabilize polymer nanolaminates,\(^5,6\) by locating at polymer/polymer interfaces. These intriguing soft materials can likewise form molecular and supramolecular networks upon microphase separation. Molecular networks develop with multiblock copolymers possessing at least one midblock capable of spanning between, and physically connecting (bridging), neighboring microdomains. Supramolecular networks, on the other hand, are nanostructural motifs that can likewise develop in multiblock copolymer systems as connected microdomain channels,\(^7-9\) which are responsible for bicontinuous morphologies.\(^10\) In this study, we consider molecular networks created by microphase-ordered bicomponent triblock copolymers consisting of glassy endblocks and a rubbery midblock. Such materials, generically regarded as thermoplastic elastomers,\(^11\) are responsible for the early commercial success of (and accompanying fundamental interest in) block copolymers. Due to their highly elastic molecular network, triblock copolymer systems are ubiquitous in a wide range of
contemporary applications, including technologies requiring highly stretchable wires for flexible electronics,\textsuperscript{12} nanostructured membranes for fuel cells,\textsuperscript{13} deformable micromolded substrates for microfluidics,\textsuperscript{14} high permittivity nanocomposites for sensors,\textsuperscript{15} and energy-efficient dielectric elastomers for actuators and energy-harvesting media.\textsuperscript{16-18} Here, we follow the transition from diblock copolymers, a soft materials archetype responsible for elucidating the mechanism of molecular self assembly, to triblock copolymers, another soft materials archetype in which molecular architecture enables network formation and imparts valuable macroscopic properties.

Independent experimental\textsuperscript{19,20} and theoretical\textsuperscript{21-23} investigations have long sought to relate the fraction and role of midblock bridging to bulk mechanical properties in molecularly symmetric copolymers in the melt, as well as in the presence of one or two solvents.\textsuperscript{24} To monitor the transition from an AB diblock copolymer with a B tail tethered at a single junction to an ABA triblock copolymer with a B midblock tethered at both ends (to form a bridge or loop), Hamersky \textit{et al}.\textsuperscript{25} have examined the phase behavior of designer A\textsubscript{1}BA\textsubscript{2} triblock copolymers synthesized from parent A\textsubscript{1}B diblock copolymers and possessing different numbers of repeat units in the A\textsubscript{1} and A\textsubscript{2} endblocks (N\textsubscript{A1} and N\textsubscript{A2}, respectively). Their results reveal that the order-disorder transition temperature (T\textsubscript{ODT}) first decreases as the A\textsubscript{2} block is initially grown and then increases upon further progression. To relate molecular asymmetry to the distribution of A segments in the endblocks, we define $\tau$ as $N_{A1}/(N_{A1} + N_{A2})$, in which case the minimum in T\textsubscript{ODT} occurs at a copolymer-specific asymmetry value (denoted $\tau^\ast$). The minimum in T\textsubscript{ODT} conversely relates to a maximum in $(\chi N)_{ODT}$, where $\chi$ represents the Flory-Huggins interaction parameter and $N = N_{A1} + N_{A2} + N_B$ ($N_B$ represents
the number of repeat units comprising the midblock). Although several theoretical models have been proposed to explain the phase behavior of such copolymers, the Mayes-Olvera de la Cruz (MOC) theory, which extends the fluctuation theory of Fredrickson and Helfand, has been successfully used, along with on-lattice Monte Carlo (MC) simulations, to quantitatively predict such unexpected phase behavior on the basis of thermodynamic considerations. While changes in molecular asymmetry also manifest differences in copolymer nanostructure and bulk properties, the dependence of midblock bridging on \( \tau \) has only been indirectly inferred thus far. In this work, theoretical and simulation methods are used in concert to (i) discern the molecular origin of \( \tau^* \), as well as fundamental relationships between \( \tau \), midblock conformations and bulk phase behavior, and (ii) transcend earlier studies devoted exclusively to either AB diblock or ABA triblock copolymers by establishing a molecular-level connection between these two important soft material archetypes.

### 6.3 Computational Methods

Details of the MOC theory are provided elsewhere, whereas the self-consistent field theory (SCFT) employed here is based on the framework developed to predict the bridging fraction in molecularly symmetric (ABA) triblock copolymers with \( N_{A1} = N_{A2} (\tau = 1/2) \). For this same case, dissipative particle dynamics (DPD) have been previously applied to interrogate triblock copolymer phase behavior and dynamics. The DPD simulations conducted here use systems containing 1000 molecules ranging in length up to 112 connected beads (each bead equates to ~0.33 kDa) in conjunction with the LAMMPS
software suite$^{34}$ and the coarse-grained parameterization described by Groot et al.$^{35}$ The pairwise interaction energy between segments $i$ and $j$ ($i,j = A$ or $B$) is designated as $\varepsilon_{ij}$ with $\varepsilon_{AA} = \varepsilon_{BB} = 25kT$ and $\varepsilon_{AB} = 50kT$, where $k$ is the Boltzmann constant and $T$ denotes absolute temperature. To differentiate among the three midblock classifications (bridges, loops and dangling ends, or simply dangles, as schematically depicted in Figure 1a) in moderately segregated copolymers after thermal equilibration at 100°C, we implement an analysis strategy based on 3D density-based clustering,$^{36}$ since simplifying assumptions at strong segregation are not valid. The MC simulations utilize a cooperative motion algorithm performed on a face-centered cubic lattice, as detailed earlier.$^{30}$ The simulation box size is chosen to fit the copolymer chain, and all lattice sites within the box are completely filled with chain segments (each translating to ~1 kDa in this study) so that the movement of a single segment necessitates the cooperative motion of other segments. The pairwise interaction energies are given by $\varepsilon_{AA} = \varepsilon_{BB} = 0$ and $\varepsilon_{AB} = \varepsilon = \chi kT/(z - 2)$, where $z (= 12)$ represents the coordination number. Each simulation is thermally equilibrated at $T^* (= kT/\varepsilon)$, and parallel tempering$^{37}$ overcomes local free energy minima at low temperatures (with long relaxation times).

6.4 Results and Discussion

As alluded to above, $T_{ODT}$ exhibits a pronounced minimum at a composition-dependent asymmetry value (denoted $\tau^*$) as $\tau$ decreases from unity and the A$_2$ endblock is grown. This macroscopic phenomenon can be explained in terms of a dilution effect: short A$_2$ endblocks are insufficiently incompatible to microphase-separate and remain mixed in the midblock-
rich matrix, thereby reducing the effective incompatibility between the A_1-containing microdomains and the matrix. In Figure 1b, values of (χN)_{ODT} evaluated at τ^* and hereafter identified as (χN)^*_{ODT} are presented as a function of the composition of the parent AB copolymer (expressed as β, where β = N_B/N_A1). For copolymers composed of styrenic endblocks and an isoprenic midblock, the composition dependence of (χN)^*_{ODT} exhibits a lower limit at β ≈ 1.8, below which τ^* cannot be discerned. Included in Figure 1b are corresponding predictions for τ^*, which is found to increase monotonically with increasing composition asymmetry, signifying that a relatively short A_2 endblock can induce the minimum in T_{ODT}(τ) if the B midblock is sufficiently long relative to the A_1 endblock. Prior experimental data^25 displayed in this figure validate the predicted composition dependence of τ^*. To relate this result to the conformational properties of the copolymer, we now seek to determine the molecular origin of τ^*. Following the concept originally proposed by Matsen,^28 the initial reduction in T_{ODT} as τ decreases from unity can be attributed to short A_2 blocks remaining mixed as dangles within the B matrix due to a low enthalpic penalty relative to the corresponding entropic gain. As the A_2 block is progressively grown, a critical block mass is reached at which the enthalpic penalty is sufficient to promote microphase separation of the A_2 blocks and, thus, co-location of nearly all the A_1 and A_2 blocks with few dangling A_2 blocks. The value of τ^* is therefore attributed to the transitional condition wherein each B midblock transforms from a dangle with one tethered end to a bridge or loop possessing two tethered ends.

To discern how this conformational evolution proceeds, DPD simulations have been
conducted on a styrene-isoprene copolymer (9 kDa A₁-endblock and 45 kDa midblock, hereafter referred to as 9-45-A₂) and analyzed to discern how the fractions of bridges (f_B), loops (f_L) and dangles (f_D) vary with molecular asymmetry. These results, presented in Figure 2a, reveal that f_B and f_L both initially increase, while f_D decreases, with decreasing τ and then reach plateau levels. Two important aspects of these results merit discussion. The first is that the bridging and looping fractions increase almost linearly as a short A₂ endblock is grown on each copolymer molecule, indicating that flowered A-rich micelles with looped midblocks, as well as loosely connected micellar clusters (flocs), develop during this initial stage. A relatively sharp transition occurs when an equilibrium network forms and these fractions become independent of τ. At τ lower than this point, the population of dangles is almost negligible (< 5%), and f_B and f_L remain nearly constant (≈ 0.59 and 0.37, respectively). From the regressed lines drawn in Figure 2a, the network-formation transition occurs at a critical τ (τ_c) of ≈ 0.87, which is higher than the experimental value reported²⁵ for τ⁺ (0.79). While this disparity likely reflects a difference in segregation strength and/or the finite nature of the simulations, the observation that the fractions initially change (in nearly linear fashion) with decreasing τ is significant and reveals that the onset of network formation, not molecular bridging, is responsible for the transition at τ_c. Figure 2b shows values of f_B and f_L calculated from SCFT (initial parent diblock χN = 70) for a 9.4-46-A₂ copolymer (to match previous experimental conditions²⁵) subject to the constraint that f_B + f_L = 1 (since values of f_D cannot be discerned from SCFT). Over the range extending from τ = 0.7 to τ = 0.5, f_B and f_L remain relatively constant at 0.61 and 0.39, respectively, which agree
favorably with the DPD simulations in Figure 2a. As $\tau$ is increased beyond 0.7, $f_B$ decreases, while $f_L$ increases, slightly until the sharp two-dimensional $A_2$ distributions used to extract $f_B$ and $f_L$ start to become diffuse, thereby preventing further quantitation of $f_B$ and $f_L$. In Figure 2b, the transition point identifies the onset of network formation at $\tau_c = 0.78$, which is in good quantitative agreement with $\tau^*$. At larger values of $\tau$, SCFT is inapplicable due to the presence of dangles, and so the DPD trends observed in Figure 2a are included to offer a complete picture of how the midblock conformations change with $\tau$.

Included in Figure 2b is a set of MC simulation results obtained from a 9-45-4 copolymer at $T^* \approx 3$, demonstrating good agreement with the SCFT prediction for $f_B$. The value of $f_L$ from the simulations is slightly lower than that predicted by SCFT because the simulations account for dangles, whereas SCFT does not. Also shown in this figure is the predicted dependence of $\tau_c$ on the parent diblock $\chi_N$. If the number of repeat units in the parent AB copolymer is held constant (as in the 9.4-46-$A_2$ series), then changes in the parent diblock $\chi_N$ relate to temperature, thereby revealing that $\tau_c$ depends not only on composition but also on temperature. It immediately follows that, since $\chi \sim 1/T$, $\tau_c$ is predicted to increase with decreasing temperature, which is confirmed by MC simulations. If this is the case, then it also stands to reason that the midblock fractions depend on temperature, which is confirmed by the MC simulation results shown in Figure 3 for a 9-45-4 copolymer. At low $T^*$, $f_B$ varies relatively little (between 0.57 and 0.62) and then decreases significantly (to below 0.30) as $T_{\text{ODT}}$ is approached. Concurrently, $f_L$ decreases slightly (from ~0.38 to 0.32) with increasing $T^*$, but then increases close to 0.50 near $T_{\text{ODT}}$. Lastly, $f_D$ remains negligibly small ($\approx 0.05$) at
low $T^*$ and then monotonically increases with increasing $T^*$. The simulation results presented in Figure 3 collectively show that increasing temperature only slightly affects midblock conformations at conditions far removed from $T_{ODT}$. As $T_{ODT}$ is approached, however, $f_B$ decreases substantially, and the copolymer network consequently weakens, in favor of increased populations of both loops and dangles. On the basis of these results, we select $T^* = 5.8$ in the following section as the highest temperature still sufficiently far from $T_{ODT}$ to avoid significant changes in the conformational fractions described above.

Thus far, only isomorphic copolymer systems have been considered in terms of variable $\tau$ or $T^*$. Figure 4 displays the effect of simultaneously varying molecular asymmetry ($\tau$) and parent diblock composition ($\beta$) on the phase behavior of $A_1BA_2$ triblock copolymers in the form of an isothermal phase diagram generated from MC simulations. All the classic (lamellae, hexagonally-packed cylinders and body-centered cubic spheres) and complex (gyroid) equilibrium morphologies typically associated with microphase-ordered diblock or bicomponent triblock copolymers are evident. Isolated regions of metastable perforated lamellae, which might turn out to be lamellae or gyroid, are also observed. These results confirm that an increase in the length of the $A_2$ block, and a corresponding reduction in $\tau$ from unity, at constant $\beta$ not only initiates midblock bridging but also provides an alternative route by which order-order transitions (OOTs) can proceed in block copolymers. Endblock asymmetry can likewise help promote the formation of copolymer vesicles in the presence of an endblock-compatible matrix-forming species. When $\tau < \tau_c$ and the $A_2$ blocks predominantly co-locate with the $A_1$ blocks, they form a bidisperse brush insofar as $N_{A1} \neq N_{A2}$. As a single-molecule route to such brushes in confined nanoscale environments, the
A$_1$BA$_2$ design provides valuable insight into the conformational aspects of network-forming copolymer architectures$^{40}$ and the molecular-level effect of bidisperse chain packing on interfacial curvature and corresponding copolymer phase behavior (cf. Figure 4) without resorting to physical blends, as well as fundamental relationships between molecular architecture and macroscopic properties.

6.5 Acknowledgments

This work was supported by the Nonwovens Cooperative Research Center at North Carolina State University. Some SCFT calculations were performed on SHARCNET, whereas the simulations were conducted at the NC State High-Performance Computing Center (DPD) and the Poznan Computer and Networking Center (MC), respectively. Support from the Polish Ministry of Science and Higher Education (Grant N204 125039) is gratefully acknowledged. One of us (R. J. S.) is also grateful for financial support from the Lars Onsager Professorship at NTNU.
6.6 References


**Matter** **2011**, *7*, 1651.


Mining, 1996, 226.


Figure 6.1. In (a), schematic illustration of triblock copolymer micelles depicting bridges, loops and dangles (labeled). In (b), predicted values of \( (\chi N)_{ODT} \) at which \( T_{ODT}(\tau) \) displays a minimum for \( A_1BA_2 \) triblock copolymers varying in molecular asymmetry as a function of the parent diblock composition (\( \beta \), solid line). Included in (b) is the dependence of \( \tau^* \) on \( \beta \) (dashed line), along with prior experimental data (O). The dotted vertical line identifies the point below which \( \tau^* \) is no longer observed. The illustrated molecules correspond to \( \tau = 1 \) and \( \tau = \frac{1}{2} \) (labeled).
Figure 6.2. DPD (a) and SCFT (b) results showing how the fractions of bridges, loops and dangles ($f_B$, $f_L$ and $f_D$, respectively; labeled) vary with molecular asymmetry ($\tau$). The lines in (a) are linear regressions to the data and serve as guides for the eye. The solid lines in (b) connect the data, whereas the dashed lines are trends inferred from the DPD outcomes in (a). Included in (b) are results from MC simulations ($f_B$, $f_L$, $f_D$) for a 9-45-4 copolymer, as well as the variation of $\tau_c$ with $\chi N$ of the parent diblock copolymer from SCFT (inset).
Figure 6.3. Dependence of the midblock fractions calculated from MC simulations on reduced temperature ($T^*$). The ODT is labeled, and the error bars correspond to the standard deviation in the data.
Figure 6.4. Isothermal phase diagram along the $\tau$-$\beta$ plane constructed from MC simulations. The morphologies are labeled: lamellae (L), perforated lamellae (PL), gyroid ($Q_{1a3d}$), hexagonally-packed cylinders (HPC), and body-centered-cubic spheres ($Q_{1m3m}$).
Chapter 7

Conclusions and Future Work

7.1 Conclusions

In this dissertation we determined how to achieve thermally activated shape-memory by physical design using melt-spinning of thermoplastic elastomers and compatible homopolymers. Firstly, we demonstrated the concept of combining the network forming element and the responsive elements of a shape memory polymer material by physical processing techniques. We hypothesized that a thermoplastic elastomer which is stable in a physically cross-linked network beyond the softening temperature of the responsive element (polyolefins in our case) will be able to retract the whole structure to the original shape upon heating. Likewise, a polyolefin (LLDPE) that was thermodynamically compatible with the midblock of a triblock copolymer (SEBS) was co-processed using bicomponent melt-spinning to prepare sheath/core, sheath/core/core and islands in sea filaments. Secondly, using mesoscale simulations we have investigated several scenarios of homopolymer/triblok copolymer blend systems with varying incompatibilities to understand the interfacial behavior and network stability of the copolymer component. This combined approach can be applied to a variety of both physical network formers and switching elements to enable a platform for manufacturing scalable shape-memory polymer systems.
7.1.1 Melt-Spun SEBS/LLDPE Bicomponent Filaments Exhibiting Versatile Shape-Memory Behavior

The shape memory behavior was achieved with commercially relevant triblock copolymer SEBS and polyolefin LLDPE prepared via melt spinning. The bicomponent filaments in sheath/core and sheath/core/core cross sections exhibited excellent shape recovery when heated to 70°C. Interesting surface morphologies resulted in the sheath/core filaments when loading at ambient temperatures. Alignment in the LLDPE component along the fiber axis resulted in the fixity of a shape at ambient temperatures. Increased crystalline and amorphous orientation was observed to cause this effect in filaments with lower LLDPE content. The shape memory behavior with heated and room temperature programming is a robust and repeatable for many cycles. In fact we report improvement in the shape memory behavior on successive cycling of filaments.

7.1.2 Dissipative Particle Dynamics of Triblock Copolymer Melts: A Midblock Conformational Study

The microdomain recognition and quantification of the network formation via chain conformations in pure ABA triblock copolymer systems were achieved using mesoscale simulations. By adapting dissipative particle dynamics to a coarse grained model of ABA triblock copolymer chains, systems at different sizes, molecular weights, compositions and A-B incompatibilities were quantified. Microdomain recognition was achieved using a three dimensional clustering of polymer trajectories obtained from DPD simulations. In the various systems the fraction of bridging, looping and dangling ends as well as a minor fraction of
udsegregating chains indicate the strengthening of molecular network through higher bridging fractions with the increase in incompatibility and chain length. The bridging fraction was determined to be the highest (0.63) for micelles, and lowest at about 0.45 for lamellar morphologies with varying composition of the triblock copolymer.

7.1.3 Morphological and Network Characteristics of Triblock Copolymer/Homopolymer Blends: Insights from Dissipative Particle Dynamics Simulations

The methods developed thus far in recognizing the microdomains and thereby quantifying the network formation in the triblock copolymers was extended to ABA copolymer/H homopolymer blends. Simulations with varying AH, BH and AB incompatibilities were subjected to the computational analysis resulting in a comprehensive understanding of the interfacial morphologies and segregation patterns of ABA/H interfaces. The interfacial thickness was estimated to be in 6 nm – 15 nm range and depended strongly on the AH incompatibility. Increasing BH incompatibility also resulted in a weakening interfacial region in the ABA/H systems. Finally, in the simulation of experimental equivalent PE/SEBS system, bridging fraction varied linearly with the copolymer/homopolymer composition. The unsegregating chains increase rapidly with increase in the PE content penetrating the SEBS network. Looping and dangling end fractions remain fairly constant throughout the PE/SEBS composition as long as there is micelle formation.
7.1.4 Shape-Memory Behavior of Melt-Spun Bicomponent Filaments with Variable Interfacial Area

Varying composition and varying number of SEBS islands in sea were utilized to control the interfacial area between SEBS and LLDPE components in the filaments. The interfacial area between SEBS and LLDPE components in islands in sea bicomponent filaments significantly affected the shape memory behavior of the resulting filaments. Larger interfacial area caused a decrease in strain fixity ratio by about 5%. Strain recovery ratio of the filaments depicted a corresponding increase by 15% as the interfacial area increases via number islands in sea. In varying composition, the best shape memory behavior is exhibited by 60/40 SEBS/LLDPE filaments as it was hypothesized that the balance of retracting force and orientation along the fiber axis are optimum at this composition. A dramatic decrease in shape recovery ratio with decreasing SEBS content was exacerbated by successive SMP cycling of the islands-in-sea filaments.

7.1.4 Phase and Conformational Evolution of Molecularly Asymmetric Triblock Copolymers

The transition of asymmetric triblock copolymer systems with increasing third block length from a weak network to a strong network was captured using DPD simulations. Linear decrease in the bridging, looping fractions with the asymmetry parameter and a corresponding decrease in the dangling ends were observed for the asymmetric A$_1$BA$_2$ systems. The molecular fractions were estimated at varying reduced temperatures using complementary Monte Carlo simulations. A phase diagram of the asymmetric triblock systems was constructed in variation of asymmetry parameter and composition.
7.2 Recommendations for Future Work

7.2.1 Experimental Directions

The bicomponent filaments spinning resulted in opening several avenues to explore shape memory polymer fabrication by physical means. There are many possibilities to extend this work to create shape memory responsive to other stimuli such as microwave, light, pH and electromagnetic fields. Incorporation of fillers to achieve a control over the mechanical and responsive properties is an interesting direction to explore future work.

Processing of one dimensional SMP structures was demonstrated to scale up with cost effective means. Several other network formers and commercially available polymers can be studied in similar design perspectives to achieve tunable shape memory filament technologies. Similarly, two dimensional bilayer and laminate structures can be formed using different macromolecular species.

Looking ahead with the engineering aspects of using SMP filaments, several devices can be envisioned to employ SMP fixity under ambient temperature conditions. For example, two sets of such filaments can be tethered to alternatively move a joined part while one motion introduces fixation in the other. Such a reversible SMP device can function as actuators in robotics.

7.2.2 Theoretical and Simulation Avenues

The simulation studies performed in our work unveil various further directions such as the variation of A/B composition in the copolymer, molecular weight of the homopolymer and simulations to explore the mechanical aspects of ABA/H blend systems. Effect of shear,
cross link density, addition of fillers, and measurement of rate of recovery of ABA/H blends represent interesting follow up studies of this work. The domain recognition and quantification of the network formation in particle dynamics simulations can be utilized to study gels, blends and other block copolymer crosslinked systems to investigate the effect of physical association with respect to different systemic factors.

The quantification of entanglements and contribution of entanglements to the strength of the blends was not explored in this work. Modifications to DPD simulation techniques can capture and quantify the effect of cross-linking via entanglement density.
Appendix A

Demonstration of Ambient Temperature Shape-Memory of SEBS/LLDPE filaments
Appendix B

Demonstration of Conventional (heated) Shape-Memory of SEBS/LLDPE filaments
Appendix C

Python Code Utilized to Generate Molecular structures

```python
# creates tmp.data.chain file
from chainMAmod12_26_11 import chain
import random
import os

#Atomtypes: 1-pe,2-s,3-eb

compositionArray=[43]  #volume fraction of PE

sebsLength=50
peLength=50
styfr=20   # styrene content in triblock

for n in compositionArray:
    chainLength= sebsLength
    totalBeads=50000/chainLength
    rho = 3       #fix
    aspect =1     #fix
    anot = pow(totalBeads*chainLength/aspect/rho,1.0/3.0)
    print anot
    name=str(n)
    print name
    numPe=n*totalBeads/100
    fvol=float(n)/100
    comp=float(styfr)/100
    numPa=0
    numSEBS=totalBeads-numPe-numPa
    aspectPe=1 #numPe*200/rho/(anot**3)
    aspectPa=1 #numPa*200/rho/(anot**3)
    aspectSebs=1#numSEBS*200/rho/(anot**3)
    LDPEbranch=8
    mass1= "1.00"
    mass3="1.00"
    mass4="1.00"
    masses=["1 "+mass1+"  
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w2 = numPa * 235
w3 = numSEBS * 190
total = w1 + w2 + w3
half1 = (100 * (numPe * 175)) / total
half2 = (100 * (numPa * 235)) / total

print name, numSEBS, numPe, numPa
if not os.path.isdir("./" + name + "/"):  
    os.mkdir("./" + name + "/")
numBeads = totalBeads * chainLength

c = chain(numBeads, rho, 1, 1, aspect)
c.seed = 54321

c.mtype = 2
c.btype = 2
c.blen = 0.5
c.dmin = 0.5
c.id = "chain"
c.masses = masses
c.info = 0
if numPe:
    array = []
    pe = int(peLength)
    print n
    for n in range(pe):
        array.append(1)

c.pz = 0
c.pzHL = [0, 1]
c.build(numPe, peLength, array)

# TO BUILD SEBS:
if numSEBS:
    array = []
    ps = int(sebsLength * comp / 2)
    print comp
    peb = chainLength - ps - ps
    for n in range(ps):
        array.append(2)
    for n in range(peb):
        array.append(3)
    for n in range(ps):
        array.append(2)
c.pz = 0
c.pzHL=[0,1]
c.build(numSEBS,sebsLength,array)

c.write("./"+name+"/all.txt")
print "done writing"

LAMMPS DPD Run Code:

units lj
boundary p p p p

atom_style bond
read_restart L1i.rest
bond_style harmonic
neighbor 1.2 bin
neigh_modify every 1 delay 0 check no communicate single vel yes cutoff 8
pair_style dpd 1.0 1.0 1234567
#pe=1,ps=2,peb=3,ps2=2
pair_coeff 1 1 25.00 4.5
pair_coeff 1 2 43.00 4.5
pair_coeff 1 3 25.35 4.5
pair_coeff 2 2 25.00 4.5
pair_coeff 2 3 48.30 4.5
pair_coeff 3 3 25.00 4.5
#ps-ps, ps-pi, pi-pi, pi-ps2, ps2-ps2
bond_coeff 1 4.0 0.8
bond_coeff 2 4.0 0.8
bond_coeff 3 4.0 0.8
bond_coeff 4 4.0 0.8
thermo 1000
thermo_style custom step temp press etotal epair
timestep 0.05
dump 1 all custom 5000 traj3.lammpstrj type mol x y z id
fix 3 all nve
restart 10000 L1i.rest L2i.rest
run 500000
R Code to perform Clustering:

```r
whole <- read.csv(file.choose(), header = F, sep = " ", dec = ".")
colnames(whole) <- c("type", "mol", "x", "y", "z", "id")
styrene <- whole[whole$type != 2, ]
xyz <- c("x", "y", "z")
styrenexyz <- styrene[c(3:5)]
library(fpc)
clusterstry <- dbscan(styrenexyz, 0.20, MinPts = 20, method = "hybrid", showplot = 1, countmode = 1:10, 100, 1000)
styrene$cluster <- clusterstry$cluster
write.table(styrene, "Clustering/filename.txt", sep = " ", col.names = FALSE)
length(unique(styrene$mol))
library(rgl)
attach(styrene)
plot3d(x, y, z, col = 1 + cluster)
```

Python Code to Analyze the Clustering Output ‘filename.txt’ from R:

```python
from operator import itemgetter
bridge=0
dangle=0
din=[]
dcount=[]
loop=0
nseg=0
molclus=[]
aa=[]
cc=[]
molString=input('Enter the number of triblock chains:')
nmol = int(molString)
aa1=set()
cc1=set()
common=set()
blockswitch=0
from pprint import pprint
fname="cl10pPP.txt"
reader= open(fname, 'r')
line=reader.readline()
while line:
    if line:
        line1=line.split()
        mol=int(line1[2])
        bead=int(line1[6])
```
cluster=int(line1[8])
if cluster != 0:
    molclus.append([mol, cluster, bead])

line=reader.readline()
molclus.sort(key=itemgetter(0,2,1))
nonzero=len(molclus)
for i in range(1,nonzero): #{ len(molclus)):
    if molclus[i-1][0] == molclus[i][0]:
        #check if same mol-id
        if abs(molclus[i-1][2] - molclus[i][2]) < 25:
            #check if they're the same block
            if blockswitch==0:
                aa.append(molclus[i][1])
#                aa1.add(molclus[i][1])
            else: blockswitch=1
            if blockswitch==1:
                cc.append(molclus[i][1])
#                cc1.add(molclus[i][1])
        blockswitch=1
        aa.sort()
        aal=set(aa)
        cc.sort()
        cc1=set(cc)
        # = intesection(aal,cc1)
else:
    common= aal & cc1
    if len(aal) > 2 or len(cc1) > 2:
        print('WARNING: Multiple clusters in one block')
    elif len(aal) == 0 or len(cc1) == 0:
        dangle += 1
    elif len(common) > 0:
        loop += 1
    else:
        bridge += 1
    aal=set()
    cc1=set()
    common=set()
    blockswitch=0
    aa=[]
    cc=[]
    aa.append(molclus[i][1])
b = 100 * bridge/nmol
l = 100 * loop/nmol
d = 100 * dangle/nmol
total = bridge + loop + dangle
unseg = nmol - total
u = 100 * unseg/nmol
##
print(fname)
print('Bridging percentage: %.2f%%' % b)
print('Looping percentage: %.2f%%' % l)
print('Dangling percentage: %.2f%%' % d)
print('Unsegregated (both ends): %.2f%%' % u)