ELASTOMERS PHYSICALLY CROSS-LINKED BY OLIGO(β-ALANINE)

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ELASTOMERS PHYSICALLY CROSS-LINKED BY OLIGO(β-ALANINE)

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ABSTRACT

Oligomers of Nylon 3 (Oligo(β-alanine)) were used as monodisperse crystallizable hard blocks in polyisobutylene based thermoplastic elastomers.

Two molecular architectures were examined. The first was an \( \text{A}_{\text{B}} \text{A} \) three-arm block copolymer where a low molecular weight polyisobutylene (30,000 g/mol) was the B block and oligo(β-alanine) was the A block. Differential scanning calorimetry showed a glass transition temperature attributable to the amorphous polyisobutylene domains, and high temperature endotherms attributable to hydrogen bonded crystalline domains of oligo(β-alanine). Morphology was examined by transmission electron microscopy; oligo(β-alanine) formed long thin ribbon-like domains. Wide angle x-ray diffraction determined the crystalline structure of these domains was similar to Nylon 3. This finding was supported by infrared spectroscopy. The effect of temperature on dynamic mechanical properties was examined using oscillatory shear rheology. The block copolymer showed viscoelastic solid properties at lower temperature, but at high temperature transitioned to a viscous liquid. The temperature of this transition increases with oligo(β-alanine) segment length. Tensile tests showed ultimate strains of 1.5 MPa and ultimate elongation of 100 %.
To increase the ultimate tensile properties, oligo(β-alanine) blocks were grafted to a high molecular weight (400,000 g/mol) copolymer of polyisobutylene with 1.1 mol % of polyisoprene known as butyl rubber. The mechanical properties were improved having ultimate strength was as high as 20 MPa, and ultimate elongations in excess of 1,000 %. When butyl rubber was grafted with mixtures of non-associating piperidine amide groups and oligo(β-alanine)s, the piperidine grafts did not interfere with the formation of crystalline oligo(β-alanine) domains. Additionally, butyl rubber was grafted with mixtures of oligo(β-alanine)s of different lengths. When mixed, the oligomers self-sort into discrete domains based on segment length and impart improved hysteresis and tensile set properties on the polymer.
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CHAPTER I

INTRODUCTION TO PHYSICAL ELASTOMER NETWORKS

1.1 Thermoplastic Elastomers

A polymer network consists of macromolecules with chain interconnections at high enough concentrations to form a percolated network\(^1\). When these polymer chains have low glass transition temperatures \(T_g\) an elastomer network results. An elastomer is a polymer that has rubber-like properties; the ability to extend to several times its original length and then rapidly return to near original dimensions\(^2\). The chain interconnections are often of a covalent nature, which produces a network that is nearly permanent. However, in some cases, the interconnections can be intermolecular physical interactions, which result in a temporary network. These physical interactions can be hydrogen bonding, van der Waals, \(\pi-\pi\) interaction, ionic interaction, or metal-ligand bonds. Increased temperatures or solvents can be used to disrupt these interactions thereby breaking down the chain interconnections and network behavior of the system. Elastomeric networks that contain reversible chain interconnections that can be broken by heat or solvent are classified as thermoplastic elastomers (TPE)\(^2\).
1.1.1 Styrenic Block Copolymers

Styrenic block copolymers constitute one of the most important classes of commercial TPEs. They were developed by the Shell Chemical Company in 1965. They possess high tensile strength, high reversible elongation, and high resilience without the addition of any filler or chemical cross-links.³

Styrenic TPEs typically have an A – B – A type molecular architecture where the A block is polystyrene, and the B block is an elastic block. The elastic block is often polyisoprene, polyisobutylene, polybutadiene or their hydrogenated analogs. The network behavior of these systems is a consequence of the A – B – A molecular architecture and the incompatibility of the A and B blocks. When the A and B blocks are of sufficient molecular weight, microphase separation occurs. At certain A – B block ratios, discrete styrene domains are dispersed within a rubbery matrix domain of block B³. (Figure 1.1) Because of the A – B – A architecture, the soft elastomer chains of the B block are terminated at both ends by a polystyrene A domain, resulting in a three-dimensional network. (Figure 1.2)
Figure 1.1 TEM micrograph of SBS. The light spheres are polystyrene domains, and the dark matrix is polybutadiene.\textsuperscript{4}

Figure 1.2 Sketch of molecular connectivity in A – B – A block copolymers depicted in Figure 1.1
At temperatures below the $T_g$ of both the A and B blocks, the material is a stiff glassy solid. At temperatures above the $T_g$ of the A and B blocks, a viscous liquid results. Only at temperatures below the A block $T_g$ and above the B block $T_g$ does the material possess elastic solid properties. This is because above the B block $T_g$, the continuous phase composed of B can be readily deformed. Because the ends of the B block are pinned down to two different glassy polystyrene domains, the entire triblock chain cannot move translationally. The resulting material behaves as a viscoelastic solid. This is different from an A – B di-block copolymer where only one elastomer chain end is terminated in a glassy domain. A system of this type is incapable of forming a three-dimensional network.

The morphology of the A – B – A triblock systems has been studied extensively and characterized with electron micrographs. Figure 1.1 shows a morphology where the polystyrene domains are microphase separated as hexagonally packed spheres with a diameter of about 30 nm. Bishop and Davison at Shell showed that these glassy polystyrene not only act as physical cross-linking junctions, but also act as reinforcing particles. They state that the “reinforcing activity of the domain, as measured by $c$ in the Kraus equation, is about equivalent to that of a good reinforcing carbon black.” A consequence of this is that by increasing the polystyrene content (increasing the filler) the stiffness of the material is increased.

Styrenic TPEs are an elegant result of polymer thermodynamics that has given rise to an incredibly useful group of elastomers. However, a practical limit
is imposed on styrenic TPEs by the available synthetic methods used to prepare them, primarily living chain polymerizations. Living polymerizations are required because in the absence of chain termination, high degrees of functionality can be obtained, and the \( A - B - A \) architecture is achieved with only a minimal amount of di-functional \( A - B \) polymer. The small variety of monomers that can be polymerized by living chain polymerizations heavily limits the primary structures one could conceive for a styrenic TPE.

1.1.2 Segmented Thermoplastic Elastomers

Segmented TPEs are block copolymers that generally contain two major components; a hard segment and a soft segment. These segments are arranged in an alternating \( -[(A)_x - (B)_y]_n - \) sequence. To achieve this type of molecular architecture, step-growth polymerizations are generally used\(^3\). Macromonomers \( A \) and \( B \) are synthesized first and then polymerized to give the desired segment block co-polymer. This type of synthetic method affords several advantages. One of which is the diversity of macromonomers that can be utilized to construct the TPE. Some of the more common soft \( B \) segments are polyesters and polyethers. Hard segments can be polyurethanes, polyamides, polyureas, and many more.

Like the styrenic TPEs, the segmented \( A \) and \( B \) blocks are immiscible and microphase separate. However, the microstructure of segmented TPEs is generally much less defined than that of the styrenic TPEs. The hard segment domains can be crystalline or amorphous and in the case of elastomers, are dispersed within the soft rubbery matrix. All of these factors in some way affect
the bulk properties of the material and provide much room for creativity in
designing materials at a molecular level. Much work has been devoted to
understanding the effects that various morphologies and chemical structures
have on the bulk mechanical properties of segmented TPEs.

1.2 Segmented TPEs Containing Monodisperse Crystallizable Hard Segments

One particular case that is relevant to the present work and has been
studied in some depth is segmented block co-polymers with monodisperse
crystallizable hard segments that self-associate via hydrogen bonding. By
eliminating the polydispersity of the hard segments, one can expect the
monodisperse hard segments to pack neatly to form relatively uniform crystals. In
comparison, polydisperse hard segments pack to form less ordered crystalline
domains (Figure 1.3).
Figure 1.3 Schematic depiction of segmented block copolymers with monodisperse or polydisperse hard segments and their difference in crystal packing.
With such control over the hierarchical structures, the monodisperse systems lend themselves to easier study of structure-property relationships than polydisperse systems. Gaymans et al. showed that the monodispersity results in fast crystallization, sharp melting transitions, low stress relaxation, and low tensile set at relatively low strains. Many of these properties can be controlled by adjusting the hierarchical structure through changes in the hard-segment molecular structure. The following discussion will divide monodisperse crystallizable hard segments into two categories. The first includes systems that form pair-wise associations via hydrogen bonds, and the second includes hydrogen bonded systems that are not limited to pair-wise associations, but many layers of hydrogen bonding (Figure 1.4).
Figure 1.4 Illustrative sketch of pair-wise associations (left) and associations of many hydrogen bonded layers (right).
1.2.1 Monodisperse Crystallizable Pairwise – Associating Hydrogen Bonding

Hard Segments

There are reports of many different hydrogen-bonding motifs used as pairwise crosslink points in polymer networks. As shown in Figure 1.5, pairwise associating hard segments form dimeric species in the hydrogen-bonding dimension. These dimeric species have hydrogen bonding acceptors \( (A_H) \) and hydrogen bond donors \( (D_H) \). The \( A_H \) and \( D_H \) groups can be arranged on the molecule to give very specific hydrogen-bonding interactions. For example, \( x \) and \( y \) act as \( D_H \) and an \( A_H \) to form a hydrogen bonded pair as shown in Figure 1.5a. In some cases, both \( D_H \) and an \( A_H \) motifs are present in one molecular structure Figure 1.6b. These molecules are self-complementary and form H-bonded pairs with themselves.
Figure 1.5. Examples of pairwise associating motifs with the equilibrium constant, $K$, where $K = \frac{k_{\text{association}}}{k_{\text{dissociation}}}$. 

a) Molecule Y acts as a hydrogen-bonding acceptor and molecule X as a hydrogen-bonding donor.

b) The self-complimentary molecule, 2-ureido-4-[1H]-pyrimidinone.

\[
K = \frac{k_{\text{a}}}{k_{\text{d}}}
\]
Both types of structures have been used to produce or modify physical networks in various types of polymer architectures. For example, polymers with grafted units capable of hydrogen bonding,\textsuperscript{44,53} alternating copolymers containing hydrogen bonding motifs\textsuperscript{8} and triblock copolymers with hydrogen bonding end groups have been explored.\textsuperscript{47}

A representative member in the category of pairwise associating hard segments is 2-ureido-4-[1H]-pyrimidinone (UPy) (Figure 1.5b). UPy was developed by Meijer and Sijbesma\textsuperscript{9} and was first introduced to polymer chemistry as a linear supramolecular chain extender. It has been adopted by many research groups due to the very high equilibrium constant of hydrogen bond association ($K = 6 \times 10^7$ M$^{-1}$ in CHCl$_3$ at 298 K). More recently it was realized that microphase separation of the associated pair plays an important role in determining the properties of the resulting supramolecular polymer. Baaijens et al. studied segmented block copolymers with UPy hard segments and polyester soft blocks.\textsuperscript{10} They found this polymer to be a microphase separated system containing one dimensional “rod-like” crystals dispersed in the amorphous polyester phase (Figure 1.6). The bulk properties of the material display TPE behavior. By DMTA analysis (Figure 1.7), a high storage modulus is observed at temperatures below the polyester $T_g$. As the temperature increases above the polyester $T_g$ the modulus abruptly drops by roughly two orders of magnitude and then exhibits a rubbery plateau where the storage modulus is independent of temperature. At 50°C, a melting temperature is observed and the modulus drops and viscous character begins to dominate.
Figure 1.6 AFM image of UPy TPE showing evidence for rod like structures (the bar represents 100 nm). Reprinted with permission from Macromolecules. Copyright 2008 American Chemical Society.

Figure 1.7 DMA plot of a segmented block copolymer with a polyester soft block and UPy hard block showing the storage modulus $E'$, loss modulus $E''$, complex modulus $|E^*|$, and the tan (δ) on a log scale as a function of temperature in °C. Reprinted with permission from Macromolecules. Copyright 2008 American Chemical Society.
The material also displays tensile properties typical of a TPE with high weight percent of hard content, i.e. high initial modulus followed by softening and eventual failure. The morphology of this system is a direct consequence of the UPy structure. The UPy segments participate in complementary pairwise hydrogen bonding. Therefore the intermolecular associations do not grow beyond dimeric species in the hydrogen bonding direction. However, in the stacking direction, (the direction normal to the molecular plane of the (Upy)$_2$ pair) the UPy dimers can stack up to form long rod-like domains. These domains are dispersed within the amorphous matrix.

Meijer et al. demonstrated superb control over the secondary structures of UPy telechelic polymers.\cite{11} By incorporating chiral groups near the UPy moiety, the UPy crystal structure was forced into right or left handed helical structures. The handedness of the helix can be controlled by the chirality of the attached group. Meijer also demonstrated control over the crystal length (in the stacking direction) by incorporating stronger or weaker hydrogen bonding groups near the UPy. With such control, these types of materials can be tuned to have very interesting properties such as stimuli responsiveness or self-healing.\cite{12}

As stated above, UPy is a pairwise associating motif. As a result, the crystalline domains and consequentially the morphology are restricted to one dimension. To allow for two-dimensional crystal growth, the pairwise motif must be abandoned for one that allows the hard segments to crystalize in two dimensions.
1.2.2 Monodisperse Crystallizable Hard Segments With Ribbon Like Morphologies

Ureas, amides, and urethanes can hydrogen bond in two dimensions, as oppose to the pairwise association mentioned above by acting as both hydrogen donors and acceptors as shown in Figure 1.8. The strength of the hydrogen bonding capability of these groups in increasing order is urethane < amide < urea. A general trend is observed that as the hydrogen bonding strength increases so does the strength of the hydrogen bonded crystalline domain. This is manifested as higher melting points, higher resistance to solvents, and deformation. The soft B blocks in these systems can range from totally amorphous polymers with low or high glass transition temperatures to semi-crystalline polymers with low or high melting temperatures. With this much variability, materials with a wide array of mechanical responses have been reported. Much of the following discussion will focus on the extensive work by Reinoud J. Gaymans et al. on segmented and triblock copolymers with monodisperse crystallizable hard segments.
Figure 1.8 Association of a polyamide (Nylon 3) to form extended hydrogen bonded structures.
1.2.2.1 Morphology and Crystal Structure

Segmented and triblock copolymers with monodisperse crystallizable hard segments tend to form morphologies with long thin ribbon-like crystalline domains. An example of this morphology is shown in the TEM image in Figure 1.9. The polymer used here is a segmented copolymer with a polypropylene soft block and an aramid hard block. The specimen was prepared by casting a thin film from solution followed by annealing. The TEM image shows aggregates of long ribbon like structures with lengths of 2 – 5 µm, and widths of ~ 100 nm. Other studies of segmented copolymers with monodisperse crystallizable hard segments have shown similar morphologies.\textsuperscript{20–25}

The structure of the crystalline domain in TPEs with monodisperse crystallizable hard segments has been explained by Barr et al. and is illustrated in Figure 1.9.\textsuperscript{26} The crystals grow in two directions; the hydrogen bonding direction (a) and in the stacking direction (b).\textsuperscript{26} Because of the anisotropic crystallization kinetics, the crystallization in the hydrogen bonding direction (a) is much faster than in the stacking direction (b). As a consequence, the (a) dimension is much larger than the (b) dimension. In the chain direction (c) there is no packing of the hard segments. As a result, the length in the (c) direction is restricted to the chain length of the hard segment. When the hard segments are monodisperse, the resulting crystal thickness in the (c) direction is uniform.
Figure 1.9 TEM micrograph of a cast thin film of $\ldots$-[PEO-PPO-PEO-T(6T)$_x$]-$\ldots$ where $x = 2$. The molecular structure is shown at the right.$^{27}$

Figure 1.10 An illustrative representation of the morphology of crystalline ribbons of a segmented block copolymer with monodisperse hard segments.$^{26}$ Reprinted with permission from Journal of Macromolecular Science Part B -- Physics. Copyright 1975 American Chemical Society.
1.2.2.2 Thermomechanical Properties and the Effect of Monodispersity

The effect of the monodispersity in the hard segment is clearly observed by examining the thermomechanical properties measured by dynamic mechanical analysis. Gaymans and Niesten did an interesting study that compares the thermomechanical properties of polyetheresteraramides containing aramid units of uniform lengths (Figure 1.11) with several commercially available segmented copolymer TPEs that have hard segments of non-uniform length.\textsuperscript{15} The polymers compared in this study are shown in Table 1.1
Table 1.1 Polymer Used in a Comparative Study of Mono vs Polydisperse Hard Segments

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Monodisperse</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Arnitel EL550</td>
<td>Copolyetherester</td>
<td>No</td>
</tr>
<tr>
<td>*Arnitel EM400</td>
<td>Copolyetherester</td>
<td>No</td>
</tr>
<tr>
<td>*Desmopan 955u</td>
<td>Polyurethanes</td>
<td>No</td>
</tr>
<tr>
<td>*Desmopan KU - 8762</td>
<td>Polyurethanes</td>
<td>No</td>
</tr>
<tr>
<td>Aramid – PTMO$_{1000}$</td>
<td>Copolyetheraramid</td>
<td>Yes</td>
</tr>
<tr>
<td>Aramid – PTMO$_{2000}$</td>
<td>Copolyetheraramid</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Denotes commercial TPEs

Figure 1.11 The storage modulus G' (MPa) versus temperature for (a) Arnitel EL550; (b) Arnitel EM400; (c) Desmopan 955u; (d) Desmopan KU-8762; (e) Aramid–PTMO$_{1000}$; and (f) Aramid–PTMO$_{2000}$. The structure of polyetheresteraramides containing aramid units of uniform lengths is shown at the top.\textsuperscript{15}
The DMA analysis in Figure 1.11 shows the storage modulus $G'$ as a function of temperature for two grades of the commercial copolyesterether, and polyurethane, and two variations of the monodisperse aramid – PTMO. These two variations differ by their respective weight percent of hard content. The first striking difference when comparing the TPEs of the same type is the increase in the modulus of the rubbery plateau. The stiffness of the rubbery plateau increases with the weight percent of hard segment. This increase in modulus is a result of an increase in the volume of hard segments and the effective physical crosslinking density because of a decrease in soft segment concentration. The second thing that should be noticed is the effect of the hard segments on the $T_g$ of the soft segments. The Arnitel and Desmopan samples show an increase in $T_g$ with increase in hard segment content. This is a consequence of the incomplete microphase separation between the A and B blocks. As the hard content increases (or the soft segment length decreases), more of the hard segment becomes mixed in the soft domain shifting the $T_g$ of the soft segment to a higher temperature. It is commonly observed in systems where microphase separation is incomplete that the soft block $T_g$ shows a dependence on the concentration of hard block. However, this shift in $T_g$ is not observed in the case of the monodisperse aramid copolymers. The absence of this shift is attributed to nearly complete phase separation of the hard and soft segments in the case of the monodisperse aramid copolymers.

Now rather than focusing on the differences between the polymers of the same type, the discussion will focus on the differences between the aramid
copolymers (they have monodisperse hard segments) against the four commercial copolymers (they have polydisperse hard segments). The polydisperse samples show more broad glass transitions and temperature dependent rubber plateau moduli. The monodisperse aramid samples show sharper glass transitions and the rubber plateau moduli show much less dependence on the temperature. Both of these differences can be explained by the near complete phase separation of the monodisperse samples. The narrowness of the melting temperatures should also be noted. The monodisperse samples show more pronounced, sharper melting temperatures. This is a consequence of the uniform thickness in the crystalline lamellae. In general, the melting temperature of crystalline polymers is dependent on lamellar thickness, with all things being equal.28

1.2.2.3 Tensile Properties and Their Relationship To Morphological Changes

The tensile properties of copolymers with monodisperse hard segments have also been examined. Gaymans et al. has shown that much of the tensile behavior can be tied directly to the morphology of the system and to changes in the morphology as the sample is deformed.23,13,29 Figure 1.12 shows stress strain plots for copolyetheresteramide (ТФТ – PTMO) samples that were prepared as extruded threads and tested in tension at strain rate of 250 mm/min. The structural information and experimental results for each of the samples is shown in Table 1.2.
Figure 1.12 A stress strain plot of the TΦT – PTMO polymers shown in

Table 1.2.  

<table>
<thead>
<tr>
<th>Polymer</th>
<th>TΦT (wt%)</th>
<th>Soft segment (g/mol)</th>
<th>σ_y (MPa)</th>
<th>σ_b (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TΦT-PTMO_{1000}</td>
<td>23</td>
<td>1000</td>
<td>9.8</td>
<td>38.1</td>
</tr>
<tr>
<td>TΦT-PTMO_{2000}</td>
<td>13</td>
<td>2000</td>
<td>5.7</td>
<td>51.9</td>
</tr>
<tr>
<td>TΦT-PTMO_{2900}</td>
<td>9.6</td>
<td>2900</td>
<td>3.4</td>
<td>58.8</td>
</tr>
</tbody>
</table>

σ_y: Yield Stress, σ_b: Fracture Stress
All three samples display a high initial modulus followed by a yielding at roughly 100% strain indicating that some structure within the material is broken up at this point. When comparing the yielding behavior of the three samples, the yielding is more pronounced in the samples with shorter soft segments and higher weight percent hard segments. To illustrate this further, Figure 1.1 shows the yielding stress $\sigma_y$ as a function of hard segment weight percent. The $\sigma_y$ has a linear relationship with the weight percent of the hard content, and because the hard segments of these samples are essentially totally crystalline, it can be said that $\sigma_y$ increases linearly with sample crystallinity.

Meijer et al. used IR – dichroism to examine the orientation of the hard segment crystallites in segmented block copolymers under strain.\textsuperscript{20,30,31,32} This method is particularly useful for systems with monodisperse urea or amide hard segments because they are highly crystalline and their C=O and N-H absorbance bands are very sensitive to hydrogen bonding structures. Segmented copoly(ether urea) were studied where the soft segment was poly(tetramethylene oxide) and the monodisperse hard segment was a bisurea butylene.\textsuperscript{20} As illustrated in Figure 1.14, before any strain is applied to the sample, both the hard and soft segments show no measurable orientation. At low strains below the yield point, the hard segments show main chain alignment perpendicular to the deformation axis. This means that the thin ribbon like crystals are aligning parallel to the deformation.
Figure 1.13 Yield stress ($\sigma_y$) versus TΦT content. \(^{29}\)

Figure 1.14 Illustrative representation of the deformation of the ribbon like crystallites at various strains. \(^{29}\)
At this point, the chains of the soft segment are only slightly aligned along the deformation axis. Increasing the strain results in continuous orientation of the soft segments. The hard domain changes dramatically from being oriented perpendicular to the deformation axis to being oriented parallel to the deformation axis. Keeping in mind that at this point in the stress strain behavior, the sample has undergone yielding, which is an indication of structure break up in the sample. One would expect that not only would the orientation of the crystals change, but also the crystal size would decrease. Meijer et al. showed that this indeed is the case by using 2D-SAXS and AFM. Before deforming these samples, the ribbon like crystals are on average 500 nm long. After deforming the samples, these crystals were on average 5 nm long. It should also be noted that after deforming the samples to a strain of 700% and then releasing the stress, the soft segments return to an unoriented state, but the hard segments remains oriented.

1.2.2.4 Mechanical and Elastic Properties

Gaymans and Schuur studied the effect of overall hard segment weight percent and hard segment length on the mechanical and elastic properties of copolyetheresteramides.\textsuperscript{27} The structure of this polymer is shown in Figure 1.11 and a summary of the structural information and mechanical responses are shown in Table 1.3. This polymers discussed here differ from the polymers discussed in Section 1.2.2.2 in that, the soft segment molecular weight is held constant while the hard segment length changed. By doing this, the effect of the
hard domain size can be isolated from the effect of the changes in crosslink density.

An increase in the hard segment length (at constant soft segment length) results in a dramatic increase in $E_{10\%}$. This is due to the reinforcing effect brought about by the amide crystallites. The percent yield strain ($\varepsilon_y$) seems to show a dependency on the length of both the soft and hard block. As the PPO block gets shorter, the $\varepsilon_y$ gets lower. This is the expected behavior for changes in soft block length. The $\varepsilon_y$ follows the opposite trend for the hard block. As the crystalline block gets larger, the $\varepsilon_y$ increases. This corresponds to a higher yield stress. In other words, the larger crystalline blocks can withstand higher stresses before beginning to break up. This becomes more apparent when taking a close look at the compression set (CS) and tensile set (TS) values.

An increase in the hard segment length (at constant soft segment length)

### Table 1.3 Mechanical and Elastic Properties of $-[\text{PEO-PPO-PEO-T}(6T)_x]-n$-

<table>
<thead>
<tr>
<th>Amide Segment</th>
<th>PEO-PEO-PO (g/mol)</th>
<th>T(6T)$_x$ (wt %)</th>
<th>$E_{10%}$ (MPa)</th>
<th>$\varepsilon_y$ (%) $^a$</th>
<th>CS (%)</th>
<th>TS$_{50%}$ (%)</th>
<th>Hyst$_{50%}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T6T</td>
<td>1</td>
<td>4000</td>
<td>7.6</td>
<td>0.69</td>
<td>64</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>T6T6T</td>
<td>2</td>
<td>4000</td>
<td>12.6</td>
<td>14</td>
<td>74</td>
<td>7.0</td>
<td>14</td>
</tr>
<tr>
<td>T6T6T6T</td>
<td>3</td>
<td>4000</td>
<td>17.1</td>
<td>21</td>
<td>_$^b$</td>
<td>8.1</td>
<td>_$^b$</td>
</tr>
<tr>
<td>T6T</td>
<td>1</td>
<td>2300</td>
<td>11.9</td>
<td>1.7</td>
<td>57</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td>T6T6T</td>
<td>2</td>
<td>2300</td>
<td>19.3</td>
<td>31</td>
<td>67</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>T6T6T6T</td>
<td>3</td>
<td>2300</td>
<td>25.5</td>
<td>29</td>
<td>_$^b$</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>T6T</td>
<td>1</td>
<td>1000</td>
<td>22.9</td>
<td>7.4</td>
<td>28</td>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>T6T6T</td>
<td>2</td>
<td>1000</td>
<td>34.3</td>
<td>56</td>
<td>40</td>
<td>17</td>
<td>_$^b$</td>
</tr>
<tr>
<td>T6T6T6T</td>
<td>3</td>
<td>1000</td>
<td>42.8</td>
<td>85</td>
<td>_$^b$</td>
<td>13</td>
<td>_$^b$</td>
</tr>
</tbody>
</table>

$^a$ Determined by Considere method.

$^b$ Not determined

27
Compression set is a measure of the viscoelastic and plastic deformation that a material undergoes after being compressed for extended periods of time. Low set means high elastic behavior and high set means high plastic behavior. Table 1.3 shows that set increases with soft segment length. This again is commonly observed for these types of systems.\textsuperscript{18,33,34} There is a unique distinction that must be made between the CS behavior with respect to total hard segment content and hard segment length. As the total hard segment content is increased, the CS increases (increases flow of the crystalline domain). This again is not terribly surprising.\textsuperscript{18,33,34} However, what is unique is the decrease in CS that is observed with an increase in modulus when the length of the hard block is increases. This is very advantageous because there are not many methods to increase a TPEs modulus and decrease CS simultaneously. This phenomenon is analogous to $\varepsilon_y$ behavior discussed above. The basic principal that emerges is that in the case of a monodisperse crystallizable hard segment, a longer hard segment is more resistant to flow and give rise to a more elastic material.

To confirm the unique results found when examining the CS behavior of these polymers, the TS of was examined through cyclic loading and unloading experiments. Figure 1.15 shows the TS as a function of strain for three samples where the soft block molecular weight is held constant.
Figure 1.15 Tensile set as a function of applied strain $TS$ as a function of the applied strain for $-[PEO-PPO-PEO_{2300-T(6T)_{2300}}]_n$ copolymers: (●) $x = 1$, (△) $x = 2$, and (■) $x = 3$.\textsuperscript{27}
All three samples initially show a sharp increase in TS and then a leveling off after \( \sim 25 \% \) strain. In the \( x = 2 \) sample the second increase in TS is attributed to strain crystallization of the soft segment. With increasing hard segment length, the TS is decreased despite higher modulus at each corresponding strain. The values for TS\(_{50\%}\) are shown in Table 1.3 and follow the same trend as the CS values. This is further conformation that longer hard segments are more resistant to flow and a more elastic material is obtained with a longer hard segment.

Work in the area of segmented copolymers with monodisperse crystallizable hard segments has shown that these types of materials can be very useful. By removing the polydispersity from the hard domains, properties that were previously inaccessible to segmented TPEs have now been attained and understood. These advances in the understanding of physical networks paves the way for the design of new and exciting materials.

1.3 Nylon 3 Oligomers as Monodisperse Crystallizable Hard Segments

Nylon 3 is a highly crystalline polyamide with a structure that allows a high density of hydrogen bonding. As a result of the high density hydrogen bonding, the crystals are very stable and resistant to most organic solvents, aqueous base solutions, and dilute aqueous acid solutions. Concentrated acids, such as formic acid, or solvents that have a strong ability to break hydrogen bonding, such as fluorinated alcohols or hot phenol, must be used to dissolve Nylon 3. Another consequence of the high-density hydrogen bonding is a high melting point that overlaps with the decomposition temperature at 340 °C.
Figure 1.16 Molecular structure of Nylon 3

When crystallized, Nylon 3 forms spherulites made of long ribbon like crystals with a thickness less than 50 Å and a length of several microns. The crystal structure of single crystals has been shown to have diffractions attributed to the antiparallel, stacked sheets in a monoclinic unit cell. \( d_{(010)} = 0.476 \text{ nm}, \ d_{(200)} = 0.400 \text{ nm}, \) and \( d_{(002)} = 0.377 \text{ nm}. \) Figure 1.17 shows the monoclinic unit cell. The chains run in the \( b \) direction and the spacing between each monomeric unit is 4.78 Å. The chains are staggered in the \( b \) direction as to allow for the C=O and H-N of adjacent chains to align and hydrogen bond at a distance of 2.88 Å (O—N distance). The \( d \)-spacing of 4.78 Å corresponds nicely with what would be expected for Nylon 3 in an extended planar zig-zag conformation. This is important because it separates the crystal structure of Nylon 3 from many other polypeptide or nylons in that the sheet like structures are flat rather that pleated. Hydrogen bonding is in the \( a \) direction with a spacing of 4.04 Å between each chain. This is also the direction of the long
Figure 1.17 The crystalline structure of Nylon 3 with \( d \) spacings in the hydrogen bonding direction \( a = 4.04 \, \text{Å} \), in the stacking direction \( b = 3.78 \, \text{Å} \), and in the chain direction \( c = 4.78 \, \text{Å} \). The chemical structure is shown in the yellow circle.
axis in the ribbon like crystals that make up the spherulites. In the stacking
direction \( c \), the chains pack in a staggered conformation with a spacing of 3.78 Å
between each chain.

The dense, strong hydrogen bonding of Nylon 3 makes it an interesting
molecule for use as a hard component in a TPE. The strength of the hydrogen
bonding could conceivably impart properties such as high resistance to solvents,
high melting points, and resistance to deformation in the hydrogen bonding
domains. Further, the strong propensity of Nylon 3 to form a single type of crystal
structure, namely stacked \( \beta \)-sheets, allows for potential uniformity in crystalline
domains in TPE copolymers. However, the high stability of Nylon 3 is a double-
 edged sword of sorts. To use Nylon 3 in a commercial application, the processes
that would be involved to manipulate the material would be impractical. One way
to harness the usefulness of Nylon 3 is to reduce the molecular weight of the
polymer.

There has been some work by Narita et al. that shows if the size of the
Nylon 3 molecules are reduced to oligomer size (2 – 5 repeat units), the solubility
can be increased, and the melting point can be decreased.\(^\text{37}\) Further, the unique
secondary \( \beta \)-sheet structure of the Nylon 3 is retained to varying degrees in the
Nylon 3 oligomers. To make a clear distinction between the high polymer of
Nylon 3, and the oligomers of Nylon 3, the oligomers will be referred to as
oligo(\( \beta \)-alanine) and the high polymer as Nylon 3 from this point forward. It is the
focus of this work to synthesize and understand the fundamental thermoplastic
elastomer behavior of networks physically crosslinked by the secondary interactions of monodisperse, crystalline, oligo(β-alanine) hard components.
2.1 Introduction

Supramolecular chemistry is an interesting field where the synthesis of molecular structures has moved beyond the covalent bond and into the controlled reversible assembly of covalent units by highly directional secondary interactions. Supramolecular chemistry can be applied to traditional covalently jointed polymers by incorporating supramolecular motifs into the covalent structure of a polymer. Segmented polyurethanes containing monodisperse or nearly monodisperse hard segments are one such case. They have displayed better microphase separation, higher crystallinity of the hard domains, higher modulus, and higher elongation and strength at break than their counterparts containing polydisperse hard segments. Gaymans and coworkers comprehensively studied stepwise synthesized monodisperse aramides as the hard segments of segmented TPEs with poly(tetramethylene oxide) as the soft segments. Compared to conventional segmented elastomers, these polymers display fast crystallization, sharp melt transitions, low stress relaxation, and low
tensile set at relatively low strains. Sijbesma and Meijer and their coworkers studied segmented TPEs based on monodisperse bisurea hard segments and poly(tetramethylene oxide) soft segments. In addition to the elastic properties, the group reported the remarkable self-sorting behavior of the bisurea hard segments with an exquisite structural alteration.\textsuperscript{11} Baaijens and coworkers incorporated quadruple hydrogen-bonding 2-ureido-4-[1H]-pyrimidinone segments into segmented polymers with amorphous polyester soft segments.\textsuperscript{10} Sogah and Shao drew inspiration from nature and synthesized and characterized silk-mimicking segmented polymers containing monodisperse alanine and alanine-glycine oligomers as hard segments.\textsuperscript{54} In addition to the main-chain segmented polymers, monodisperse hard segments, including 4-urazoylbenzoic acid,\textsuperscript{46} ureidopyrimidinone, and urea,\textsuperscript{52} have been grafted onto elastomers as side groups and are shown to be effective physical crosslinks upon microphase separation.

The above monodisperse hard segments self-associate into sheet-like supramolecular structures via cooperative hydrogen-bonding interactions. While ureidopyrimidinone forms a pairwise association, the others form extended ribbons with a high degree of association. The ribbons stack on top of each other to give the third dimension of the crystalline domains, which often display a fibrous morphology as the result of the high aspect ratio of the ribbons. The well-defined structure of the hard segment allowed small molecule model compounds to be synthesized and studied to provide the structural basis for understanding the structure of the crystalline hard domain. Insights about the structure-property
relationship are obtained due to the structural clarity of the hard segments and the domains that they form.

2.1.1 Supramolecular Triblock Copolymers

In contrast to the relatively widespread interest in monodisperse hard segments in segmented TPEs, the supramolecular motifs are only sparsely explored in TPEs of the triblock ABA type. In fact, most reports of supramolecular ABA block copolymers contain supramolecular motifs for the purpose of linear chain extension rather than controlled domain formation.\(^{39-44}\) However, Gaymans and coworkers recently expanded their study of monodisperse diaramide hard segment to triblock TPEs.\(^{13,15,17,18,31,27,42,45,55}\) The middle blocks they used were poly(ether ester) from poly(tetramethylene oxide) extended by terephthalate, and poly(ether urethane) from poly(tetramethylene oxide) extended by 4,4’-methylenebis(phenyl isocyanate). Like in the cases of segmented TPEs, the diaramide end blocks self-associate via hydrogen bonds and exist as crystalline domains with high aspect ratios. These triblock TPEs demonstrated rheological and dynamic mechanical characteristics typical to viscoelastic solids even when the diaramide hard component only accounts for as little as 3% of the weight of the material. The ultimate strength and elongation are respectable as long as the middle block has a high enough molecular weight. However, the middle blocks in the above polymers are semicrystalline at room temperature, under which condition the tensile properties were studied. Therefore, these polymers strictly speaking still possess multiple hard segments;
or at least, the mechanical properties cannot be unambiguously linked to the supramolecular diaramide domains.

The only example of a triblock copolymer with an amorphous middle block and two end segments that form supramolecular domains was studied by Stadler and coworkers. They showed that telechelic oligoisobutylene end-functionalized with 4-urazoylbenzoic acid displayed solid elastic behavior at room temperature and became a viscous liquid above the melting temperature of the 4-urazoylbenzoic acid domain. The molecular weight of the oligoisobutylene that they used was only 4,800 g/mol, substantially below the average molecular weight between entanglements. No tensile property was reported.

The scarcity of knowledge in the literature about TPEs based on supramolecular association of the end blocks clearly demands research attention in this class of materials. The structurally well-defined nature of these polymers, including the narrow polydispersity of the middle block and the supramolecular structures formed by the end block, promises to simplify the understanding of the structure-property relationship and provides immense opportunities for designing new elastomeric materials with specific sets of properties.

2.2 Project Concept

The polymers synthesized and examined in the following work are three-arm star polymers of polyisobutylene end-functionalized with monodisperse oligo(β-alanine) blocks. The polyisobutylene polymer is synthesized by living cationic polymerization and end-functionalized with methoxyaniline through a
Friedel-Crafts alkylation. This provides a primary amine that can couple with an active ester on oligo(β-alanine). The oligo(β-alanine) blocks are prepared separately by solution phase peptide synthesis techniques and are coupled to the polyisobutylene chain ends in the last step (Scheme 2.1).

Because the polyisobutylene chain is incompatible with the oligo(β-alanine) segments, microphase separation takes place. It has been found that the oligo(β-alanine) segments form ribbon like crystals that are dispersed within a rubbery polyisobutylene matrix. These crystalline domains act both as reinforcing domains and as junction points for multiple polyisobutylene chains. For this study, the polyisobutylene soft block molecular weight is held constant at 30,000 g/mol (10,000 g/mol per arm) while the oligo(β-alanine) segments range from two (z = 2) repeat units up to 5 repeat units (z = 5).
Scheme 2.1 Synthesis of oligo(β-alanine) end-functionalized polyisobutylene
2.3 Experimental

The experimental section is broken into sections describing the instrumentation used, an example of the oligomer synthesis, and an example of polymer functionalization.

2.3.1 Instrumentation Used

Nuclear magnetic resonance (NMR) experiments were performed on either a Varian Mercury 300-MHz or a Varian Avance 500 MHz instruments. Chemical shifts were determined using solvent peaks as the references.

Gel permeation chromatography (GPC) was performed at 30 °C using three tandem Waters HR styragel columns and THF as the solvent. The eluents were monitored using an inline Wyatt Dawn EOS multiangle laser light scattering (MALLS) detector and a Waters Model 2414 differential refractometer concentration detector.

Fourier transform infrared (FT-IR) spectroscopy was performed on a Digilab Excalibur FTS 3000 series FT-IR spectrometer with Win-IR Pro Software. All FT-IR spectra were collected at a resolution of 4 cm\(^{-1}\). All samples were prepared either by casting onto NaCl plates from a CHCl\(_3\) solution or hot pressing thin films above the \(T_m\) and stretching them across a NaCl plate.

Differential Scanning Calorimetry (DSC) experiments were performed on a TA instrument model Q2000 with Advantage software version 2.8.0.382. Samples between 5.00 and 7.00 mg were loaded in Tzero aluminum pans for experiments.
TGA analysis was performed on a TA instrument model Q500. Analysis was performed under both air and nitrogen atmospheres and samples were heated at a ramp rate of 10 °C/min.

For mechanical and rheological tests, all samples were hot-pressed into a 1 mm thick mold at each sample’s respective T<sub>m</sub> and slowly cooled before removing from the press. Tensile tests and stress relaxation tests were performed on a RSA3 dynamic mechanical analyzer. The specimens were prepared by cutting the above hot-pressed films into 5 mm x 15 mm strips. Tensile tests were performed at ambient temperature and were strained at a rate of 60 mm/min. Strain was calculated from clamp displacement. For stress relaxation, samples were strained rapidly to 5%, and stress was measured as a function of time at ambient temperature. For rheological testing, samples were dried out into discs with a 5 mm diameter. Small-amplitude oscillatory-shear (SAOS) frequency sweep measurements were carried out using an Advanced Rheometrics Expansion System (ARES). Measurements were made on a 5 mm diameter parallel disc cell. Polymers 4a – 4d were analyzed at room temperature, and polymer 1 was analyzed at 0 °C to stay within the torque limits of the rheometer. Frequency sweep experiments from 0.1 Hz to 100 Hz were performed on 4a from 0 °C to 50 °C at 10 °C intervals to construct a master plot according to the WLF equation and reference to 0 °C. Shift factors are plotted in APPENDIX A. Temperature sweep experiments were performed at 10 Hz and a strain amplitude of 2%.
WAXD experiments were conducted on an instrument equipped with a Rigaku 18 kW rotating anode generator and an image plate as the detector. The instrument was calibrated using silicon powders with $2\theta$ being 28.4° under Cu Kα radiation. The air scattering was subtracted. The 1D WAXD curve was integrated from the 2D image. Samples were pressed into thin films and annealed prior to the experiment.

2.3.2 Synthesis

Typical solution phase peptide coupling procedures were followed to produce the boc and benzyl protected oligo(β-alanine)s 2a – 2d.\(^{37}\)

2.3.2.1 Oligo(β-alanine) Dimer Synthesis [3a]

The synthetic steps to transform 2a to 3a are shown in scheme 2 and detailed procedures for each step are given below.
Scheme 2.2 Synthetic steps to transform 2a to 3a
Oligomer 2a (1.0 g, 2.8 mmol) was dissolved in a 4 M HCl dioxane solution (25 mL) and allowed to stir over night. The resulting slurry was pumped to dryness to give 5a as a white powder (98%, 0.80 g). \(^1\)H NMR (300 MHz; CDCl\(_3\)): \(\delta\) 8.16 – 7.99 (m, 4H), 7.62 (s, 5H), 5.04 (s, 2H), 3.51 – 3.37 (m, 4H), 2.93 – 2.79 (m, 2H), 2.57 (t, \(J = 6.6\) Hz, 2H).

Oligomer 5a (1.0 g, 4.0 mmol) was dissolved in anhydrous chloroform (25 mL) and protected with nitrogen. Next, \(m\)-toluoyl chloride (0.53 mL, 4.0 mmol) was added followed by an excess of triethylamine (1.2 mL, 9.13 mmol). The reaction was allowed to stir for one hour and was then washed three times with an aqueous 10 wt% citric acid solution. The organic solution was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure to give 6a as an off white solid (93 %, 1.37 g). \(^1\)H NMR (300 MHz; CDCl\(_3\)): \(\delta\) 7.61 (s, 3H), 7.59 – 7.52 (m, 1H), 7.39-7.26 (m, 8H), 7.22 – 7.12 (m, 1H), 6.35 – 6.23 (m, 1H), 5.12 (s, 2H), 3.72 (q, \(J = 5.7\) Hz, 2H), 3.56 (q, \(J = 6.0\), 2H), 2.59 (t, \(J = 6.3\) Hz, 2H), 2.47 (t, \(J = 6.0\) Hz, 2H), 2.39 (s, 3H).

Oligomer 6a (1.0 g, 2.7 mmol) was dissolved in methanol (50 mL) in the presence of C/Pd 10 wt% (0.1 g). A slow stream of H\(_2\) was bubbled through the solution for five hours. The suspension was then filtered to remove the catalyst, and the solvent was removed under reduced pressure at room temperature to give 7a as a white solid. (98 %, 0.74 g). \(^1\)H NMR (300 MHz; DMSO): \(\delta\) 8.43-8.34 (m, 1H), 7.99-7.91 (m, 1H), 7.62 (s, 1H), 7.61-7.55 (m, 1H), 7.34-7.27 (m, 2H), 3.42 (q, \(J = 6.0\) Hz, 2H), 3.24 (1, \(J = 5.7\) Hz, 2H), 2.40-2.29 (m, 7H).
Oligomer 7a (1.0 g, 3.9 mmol) and N,N'-Disuccinimidy carbonate (1.11 g, 4.3 mmol) were dissolved in anhydrous DMF (10 mL) under the protection of nitrogen atmosphere. Next, triethylamine (2.49 mL, 17.9 mmol) was added and the reaction stirred for three hours. The reaction solution was then diluted with 20 mL ethyl acetate. The diluted reaction solution was then washed 3 times with a 10 wt% aqueous citric acid solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure to give 3a as a white solid (58%, 0.84 g) $^1$H NMR (300 MHz; DMSO-d$_6$): δ 8.40-8.35 (m, 1H), 8.10-8.05 (m, 1H), 7.61 (s, 1H), 7.61-7.56 (m, 1H), 7.31-7.29 (m, 2H), 3.43 (q, $J = 6.6$ Hz, 2H), 3.37 (q, $J = 6.6$ Hz, 2H), 2.83 (t, $J = 6.9$ Hz, 2H), 2.79 (s, 4H), 2.35 (t, $J = 7.2$ Hz, 2 H), 2.329 (s, 3H). $^{13}$C NMR (500 MHz; DMSO-d$_6$): δ 170.7, 170.4, 170.2, 167.4, 166.3, 137.5, 134.5, 131.6, 128.1, 127.7, 124.3, 36.1, 35.4, 35.2, 34.2, 30.5, 25.5, 20.9

2.3.2.2 Oligo(β-alanine) Trimer - Pentamer Synthesis [3b – 3d]

Compounds 3b – 3d can be synthesized using similar procedures as detailed above for 3a starting from 2b – 2d, respectively. The NMR characterization data for 3b – 3d are compiled below.

3b. $^1$H NMR (500 MHz; DMSO-d$_6$): δ 8.41-8.35 (m, 1H), 8.08-8.02 (m, 1H), 7.92 – 7.87 (m, 1H), 7.62 (s, 1H), 7.61-7.56 (m, 1H), 7.31-7.29 (m, 2H), 3.42 (q, $J = 6.0$ Hz, 2H), 3.32 (q, $J = 6.0$ Hz, 2H), 3.23 (q, $J = 6.0$ Hz, 2H), 2.81 (t, $J = 7.0$ Hz, 2H), 2.79 (s, 4H), 2.36 – 2.23 (m, 5H), 2.22 (t, $J = 7.0$ Hz, 2 H). $^{13}$C{$^1$H}
NMR (500 MHz; DMSO-d$_6$): $\delta$ 170.6, 170.3, 170.1, 167.3, 166.2, 137.4, 134.5, 131.5, 128.1, 127.6, 124.2, 39.5, 36.1, 35.4, 34.2, 30.5, 25.4, 20.9.

3c. $^1$H NMR (500 MHz; DMSO-d$_6$): $\delta$ 8.43-8.35 (m, 1H), 8.09-8.02 (m, 1H), 7.93 – 7.80 (m, 2H), 7.63 (s, 1H), 7.62-7.55 (m, 1H), 7.34 - 7.29 (m, 2H), 3.43 (q, $J$ = 6.3 Hz, 2H), 3.35 (q, $J$ = 6.0 Hz, 2H), 3.28 – 3.14 (m, 4H), 2.83 (t, $J$ = 6.9 Hz, 2H), 2.80 (s, 4H), 2.37 – 2.29 (m, 5H), 2.26 – 2.14 (m, 4H). $^{13}$C{$_1$H} NMR (500 MHz; DMSO-d$_6$): $\delta$ 170.7, 170.4, 170.2, 167.4, 166.3, 137.5, 134.5, 131.6, 128.2, 127.7, 124.3, 36.1, 35.4, 35.2, 34.2, 30.5, 25.5, 20.9.

3d. $^1$H NMR (500 MHz; DMSO-d$_6$): $\delta$ 8.42-8.34 (m, 1H), 8.08-8.01 (m, 1H), 7.93 – 7.79 (m, 3H), 7.63 (s, 1H), 7.61-7.56 (m, 1H), 7.33 - 7.29 (m, 2H), 3.43 (q, $J$ = 6.0 Hz, 2H), 3.35 (q, $J$ = 6.0 Hz, 2H), 3.27 – 3.15 (m, 6H), 2.85 (t, $J$ = 7.0 Hz, 2H), 2.80 (s, 4H), 2.38 – 2.29 (m, 5H), 2.25 – 2.15 (m, 6H). $^{13}$C{$_1$H} NMR (500 MHz; DMSO-d$_6$): $\delta$ 170.6, 170.24, 170.05, 167.3, 166.2, 137.4, 134.5, 131.5, 128.1, 127.6, 124.2, 39.7, 39.5, 39.4, 36.1, 35.3, 35.2 34.2, 30.5, 25.4, 20.9.

2.3.2.3 End-Functionalization of Polyisobutylene with Oligo(β-alanine) [4a – 4d]

Polymers 4a – 4c were synthesized in an identical manner by coupling 1 with 3a – 3c, respectively. A procedure is given below using 4c as an example. Polymer 1 (1.0 g, 0.03 mmol) and 3c (0.04 g, 0.11 mmol) were dissolved in anhydrous chloroform (15 mL). The solution was refluxed for 4 days under a nitrogen atmosphere and then poured into methanol (200 mL). An off-white solvent-swollen precipitate formed. The bulk solvent was decanted, and the
residual solvent was blotted away with paper towel. The final elastomeric solid product was obtained after being dried in a vacuum oven at 60 °C overnight (97%, ~1.0 g). The $^1$H NMR spectra of 4a – 4c are shown in Figure 2.1.

The procedure for synthesis of 4d is very similar to that for 4a – 4c described above, except that a mixture of chloroform and trifluoroethanol (10:1 volume ratio) was used as the solvent. The $^1$H NMR spectra of 4d is also shown in Figure 2.1
Figure 2.1 ¹H NMR spectra of 4a – 4d, and 1 with peak assignments in CDCl₃. The baseline is expanded down field of the dashed vertical line for clarity. From top to bottom: 4d with the addition of a small amount of TFA-d, 4c, 4b, 4a, and polymer 1 with the methyl protons on the 4 - alkyl and 5 - alkyl substituted methoxy aniline telechelic denoted with **. Residual methanol is denoted with a single *.
2.4 Results and Discussions

This section is broken into a discussion of the block copolymer synthesis and primary structure, the self-association of the oligo(β-alanine) segments, thermal properties, crystalline structure of the oligo(β-alanine) domains, microphase morphology, viscoelastic properties, and mechanical properties.

2.4.1 Synthesis and Primary Structure Characterization

The ortho-methoxyaniline-capped telechelic poly(isobutylene), 1, was synthesized according to a method previously established by the Kennedy et al (Scheme 2.1). Briefly, isobutylene was first polymerized under standard living cationic polymerization conditions. The living tertiary carbocation was harnessed for Friedel-Craft alkylation of the nucleophilic ortho-methoxyaniline to give 4-alkyl and 5-alkyl regioisomers in roughly equal amounts. The oligo(β-alanine)s, 2a – 2d, were capped by a meta-toluoyl group at the N-terminus and activated by a succinimidyl ester at the C-terminus, to give 3a – 3d. Reflux of 1 and 3a – 3c in chloroform gave the target polymers, 4a – 4c, respectively. The reaction between 1 and 3d required the addition of a small amount of trifluoroethanol in order to dissolve 3d. When trifluoroethanol was not added, incomplete reaction resulted even after prolonged reaction time. Complete conversion of 1 to 4a – 4d was evident from the displacement of the methoxy peaks of 1 at δ 3.83 and 3.81 ppm in the $^1$H NMR spectrum by the methoxy peaks of 4a – 4d at δ 3.80 and 3.78 ppm (Figure 2.1). A complete assignment of the $^1$H NMR spectrum of 4c in CDCl$_3$ is made, based on chemical shifts and $^1$H-$^1$H correlation spectroscopy.
(see APPENDIX B). Assignments of the spectra of 4a and 4b were based on chemical shifts and inferred from the 4c assignments. Polymer 4d also appears to dissolve in chloroform by the naked eye. However, the $^1$H NMR resonances due to the oligo(β-alanine) segments cannot be observed in the $^1$H NMR spectrum in CDCl$_3$, indicating that the β-alanine pentamer segments remain significantly aggregated, in contrast to the dimer to tetramer. These resonances emerge in the presence of an acid such as trifluoroacid acid, which apparently breaks the hydrogen bonds in the aggregate.
2.4.2 Self-Association via Hydrogen Bonds

Infrared spectroscopy is a well-established technique to study self-association of polyamides involving inter- and intramolecular hydrogen bonding and subsequently allows inference of their solid state structures in supplement to X-ray diffraction. In particular, the crystal structure of poly(β-alanine) (i.e., Nylon 3) and the IR spectrum corresponding to that structure are known in the literature.\textsuperscript{35,36} The Jia group recently observed that polydisperse oligo(β-alanine)s adopted the same stacked β-sheet crystal structure in the solid state and reported the corresponding IR spectrum.\textsuperscript{57} Infrared spectroscopy is again used here to assess the self-association of the oligo(β-alanine) segments in 4a – 4d in bulk states as well as in solution.

Films cast from a chloroform solution onto NaCl plates were used for the IR study. Alternatively, thin films were pressed above the T\textsubscript{m} of the respective sample and then placed on top of NaCl disks. The solvent-cast specimens and the pressed specimens gave identical spectra. The self-association behavior is not dependent on the method of sample preparation within the detection limit of IR. The IR spectra of 4a – 4d and Nylon 3 are compared in Figure 2.2. The key absorptions are summarized in Table 2.1.
Figure 2.2 FT-IR spectra of 4a – 4d and Nylon 3. The vertical dash lines at 3296, 1641 and 1543 cm\(^{-1}\) are added as a guide to the eyes.

Table 2.1 FT-IR Absorbance Bands for 4b – 4d.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Amide A (cm(^{-1}))</th>
<th>Amide I (cm(^{-1}))</th>
<th>Amide II (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>3302 cm(^{-1})</td>
<td>1647 cm(^{-1})</td>
<td>1596 cm(^{-1})</td>
</tr>
<tr>
<td>4b</td>
<td>3285 cm(^{-1})</td>
<td>1638 cm(^{-1})</td>
<td>1539 cm(^{-1})</td>
</tr>
<tr>
<td>4c</td>
<td>3289 cm(^{-1})</td>
<td>1638 cm(^{-1})</td>
<td>1541 cm(^{-1})</td>
</tr>
<tr>
<td>4d</td>
<td>3289 cm(^{-1})</td>
<td>1638 cm(^{-1})</td>
<td>1541 cm(^{-1})</td>
</tr>
<tr>
<td>(β-alanine)(_{10})</td>
<td>3296 cm(^{-1})</td>
<td>1641 cm(^{-1})</td>
<td>1543 cm(^{-1})</td>
</tr>
</tbody>
</table>
Polymers 4b – 4d show amide A, amide I, and amide II absorbance bands at nearly the same wavenumbers as the Nylon 3. The amide A band at 3296 cm\(^{-1}\) is attributable to N-H stretching of hydrogen-bonded β-alanine residues. The amide I and II bands at 1641 and 1543 cm\(^{-1}\), respectively, are also attributable to hydrogen-bonded β-alanine residues. Block co-polymer 4a shows similar absorbance bands, but with a slight blue shifting of the amide II band, and a broadening of the amide I band in the higher wavenumber direction. Also, a very noticeable broadening of the amide A with the appearance of a small shoulder at 3302 cm\(^{-1}\) can be seen. A small peak at 4421 cm\(^{-1}\) can be assigned to N-H without hydrogen bonding. These shifts and the appearance of the peak at 3302 cm\(^{-1}\) are strong indicators that with only two β-alanine residues, the oligo(β-alanine) domain is not totally self-associated. This experiment provides the initial spectroscopic evidence that the oligo(β-alanine) segments completely self-associate into the β-sheet structure in 4b – 4d and perhaps partially assemble in 4a.

As a comparison infrared spectroscopy was also used to assess the self-association of polymers 4a – 4d in a solution of CDCl\(_3\). Polymers 4a – 4c were dissolved in CDCl\(_3\) and loaded into a solution FT-IR cell for analysis. The solution of 4d is still too viscous to use the solution cell. As an alternative method, 4d was dissolved in CDCl\(_3\) and placed between two NaCl discs for analysis. The solution FT-IR spectra are shown in Figure 2.3.
Figure 2.3 Solution FT-IR spectra of 4a – 4d in CDCl₃.
Polymers \(4a\) and \(4b\) are shown to be non-associating in CDCl\(_3\). They do not show a sharp amide A band below 3300 cm\(^{-1}\) but show two small peaks at 3446 and 3421 cm\(^{-1}\). The amide I peaks show a broadening and blue shift to 1663 cm\(^{-1}\), and the amide II peak shows a red shift to 1513 cm\(^{-1}\). These shifts are indicative of non-hydrogen bound species. Polymer \(4c\) is shown to be mostly non-associated with a small fraction of hydrogen bonding amide groups present. The amide A region of the spectrum shows the same two peaks as \(4a\) and \(4b\) at 3446 and 3421 cm\(^{-1}\), but also shows a small peak at 3298 cm\(^{-1}\). The amide I is at a slightly lower wave number that that for \(4a\) and \(4b\), and the amide II is again at 1513 cm\(^{-1}\). Polymer \(4d\) is nearly completely hydrogen bonded in CDCl\(_3\). The amide A region shows a large sharp peak at 3291 cm\(^{-1}\) and a small peak at 3415 cm\(^{-1}\). The amide I and II regions show only slight shifts from the solid state spectrum in Figure 2.2.

2.4.3 Thermal Study

TGA analysis was performed on polymers \(4a\) – \(4b\) to determine the decomposition temperatures of each polymer (Figure 2.4). Each polymer shows a decomposition temperature of 377 °C. The decomposition of the oligo(\(\beta\)-alanine) segments can also be observed as small steps at the onset of decomposition. The larger oligo(\(\beta\)-alanine) segments give a larger step as shown in the inset in Figure 2.4.
Figure 2.4 TGA in nitrogen of 4a – 4d with an inset
Polymer samples after chemical synthesis without any thermal or solvent treatment were used for DSC study. Endothermic peaks attributable to the melt transitions of the oligo(β-alanine) domains were observed for 4b – 4d on the first heating cycle (Figure 2.5), indicating there is a strong tendency to undergo microphase separation between the oligo(β-alanine) segments and the polyisobutylene block of 4b – 4d even without annealing. In contrast, no melt transition was detected for 4a. For 4d, the bimodal endotherms most likely
Figure 2.5 DSC trace of 4a – 4d and 1 at a heating rate of 10 °C/min. The second heating cycles are shown.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>Hard Segment (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-64.5</td>
<td></td>
<td>0.0%</td>
</tr>
<tr>
<td>4a</td>
<td>-64.8</td>
<td></td>
<td>2.6%</td>
</tr>
<tr>
<td>4b</td>
<td>-64.9</td>
<td>100</td>
<td>3.3%</td>
</tr>
<tr>
<td>4c</td>
<td>-64.7</td>
<td>188</td>
<td>4.0%</td>
</tr>
<tr>
<td>4d</td>
<td>-64.7</td>
<td>230, 237</td>
<td>4.7%</td>
</tr>
</tbody>
</table>
indicate the co-existence of two kinds of crystals. Overall, the melting
temperature (T_m) increases with the increase of the number of β-alanine residues
in the hard segment. Attempts to determine the heat of fusion failed because the
weight percent of the oligo(β-alanine) segment is too low to yield reproducible
values. The glass transition temperatures (T_g) of the polyisobutylene block were
essentially the same in 4a – 4d and the parent polyisobutylene 1.

2.4.4 Crystal Structure of Hard Domains

WAXD studies were carried out to elucidate the structures of the
crystalline oligo(β-alanine) phase. The WAXD profile of 4c is shown in Figure
2.6a. A diffused scattering peak is present at 2θ = 12°, corresponding to the
characteristic correlation length of the amorphous polyisobutylene block. For 4c,
the diffraction peaks at 2θ = 22.0° and 23.4° are clearly observed, and a third
weak diffraction is extremely weak and broad but nonetheless discernible at θ =
18.2°. These diffractions correspond to d spacing of 4.74, 3.93, and 3.70 Å and
are consistent with those in the main modification of Nylon 3 crystals as
illustrated in Figure 2.6b. This experiment confirms the results from the FT-IR
examination in section 2.4.2 that the crystalline structure for 4c is the same as
that of the Nylon 3.
Figure 2.6 a) WAXD plot for a decamer of Nylon 3 and for 4c b) an illustration of the known crystal structure for Nylon 3.\textsuperscript{35,36}
2.4.5 Microphase Morphology

Polymer 4c was used as a representative example to examine the phase morphology by TEM. A specimen obtained by casting a drop of chloroform solution of 4c on a carbon-coated copper grid was analyzed. The electron micrograph reproducibly revealed the morphology of fibrils embedded in globs of amorphous substance (Figure 2.7). The fibrous structure is better visualized after the specimen was dipped into fresh chloroform several times to dissolve away the excess material on the grid (Figure 2.7).
Figure 2.7 TEM micrographs of 4c. (left) Specimen prepared by drop-casting a chloroform solution of 4c on a grid. (right) The specimen on the left was dipped into fresh chloroform a few times.
2.4.6 Viscoelastic Properties

The frequency dependence of storage modulus (G') and loss modulus (G'') of 4a – 4d was studied at 25 °C under oscillatory shear at a shear strain amplitude of 2.5 %. Elastic behavior dominates for 4b – 4d with G' > G'' over the entire frequency window from 0.001 rad/sec to 100 rad/sec. The upturn of G'' at high frequencies indicates that the Rouse motion begins to become restricted. The rise of G'' at low frequencies can be observed for 4b, indicating that the experimental time scale is starting to approach the lifetime of the physical crosslinks as the number of β-alanine residues decreases in the hard segment. Eventually, the transition from elastic behavior to viscous behavior occurs in 4a at low frequencies, where a crossover of G' > G'' was observed.

The test temperature for polymer the unfunctionalized polymer 1 had to be lowered to 0 °C to stay within the torque limits of the rheometer when measuring polymer 1. To compare polymer 4a with polymer 1, a series of frequency sweeps at different temperatures ranging from 0 °C - 50°C at 10 °C intervals were performed. The data was then complied into a master plot according to the WLF equation and referenced to 0°C (shift factors shown in APPENDIX A). The comparison shows the reptation time for 4a (T_d) is roughly 10^2 times longer than the T_d for 1. 4a forms a transient network, within the experimental timescale, that behaves like a higher molecular weight polymer than polymer 1.
Figure 2.8 Frequency dependence of the storage modulus ($G'$) and the loss modulus ($G''$) at 25 °C for a) 4a b) 4b c) 4c and d) 4d.

Figure 2.9 Frequency dependence of the storage modulus ($G'$) and the loss modulus ($G''$) at 0 °C for a) 4a and b) a master curve of 1 reference to 0 °C.
The temperature dependence of $G'$ and $G''$ at 10 Hz with a strain amplitude of 2% were measured for polymers 4b – 4d (Figure 2.10). At low temperature, they each show an area of relative temperature independence followed by a melting transition at higher temperatures. The melting transitions correlate well to the onset of the melting endotherms measured by DSC.
Figure 2.10 Temperature dependence of $G'$ and $G''$ at 10 Hz and a strain amplitude of 2% for polymers a) 4b, b) 4c, c) 4d. $G' ($\blacklozenge$)$, $G'' ($\blacklozenge$)$, and tan $\delta$ ($\blacktriangle$)
2.4.7 Mechanical Properties

Tensile and stress relaxation properties were tested on the elastic solids, **4b – 4d**. The stress-strain curves are shown in Figure 2.11. The modulus and strength at break increase with the increase of the number of β-alanine residues in the hard segment. The strain at break did not display any trend but is generally low between 80% to 130%. Failure occurred before any significant strain-induced softening. The lack of strain-induced softening can be attributed to the insufficient number of entanglement between crosslinks. The molecular weight between crosslinks in the present cases is the molecular weight of each arm of the 3-armed star polymer, i.e., 9,700 g/mol. The relatively weak mechanical strength can therefore be partially attributed to the insufficient molecular weight between crosslinking joints.58

A stress relaxation experiment was performed on **4b – 4d** where the samples were deformed rapidly to a strain of 5% and the modulus was measured as a function of time. Two important observations can be made. First, **4b – 4d** all maintain a stress within the experimental time scale. This confirms the findings by rheology that within the experimental time window, a permanent network is achieved. The relaxation moduli follow the same trend observed in the tensile test.
Figure 2.11 a) Tensile test results for 4b – 4d. Samples deformed at 60 mm/min and strain was calculated from clamp displacement. b) Stress relaxation test results for 4b – 4d. Samples strained to an initial strain of 5%.
2.5 Conclusion

The functionalization of polyisobutylene 1 with oligo(β-alanine)s was found to result in a microphase separated system where oligo(β-alanine) segments self-associate to form discrete crystalline fibril domains. However, there appears to be a lower limit to the length of the oligo(β-alanine) segments that will result in full association of the oligo(β-alanine). When there are less than three repeat units in the oligo(β-alanine) segment, infrared spectroscopy indicates a mixture of associated and non-associated amide groups. When there are more than three repeat units in the oligo(β-alanine) segment, infrared spectroscopy indicates that the system is fully associated and has a hydrogen bonding structure very similar to that of Nylon 3.

Polymers 4b – 4d show viscoelastic properties typical of a thermoplastic elastomer. They possess a rubbery plateau that extends up to the hard block T_m. Above the hard block T_m, the G’ drops sharply as the physical network is broken up. Polymer 4a however, shows much different behavior presumably because of the incomplete association of the oligo(β-alanine) segments. At a fixed temperature (30 °C), a low frequency cross-over is observed. This cross-over corresponds to a relaxation time about 10^2 times longer than the T_d observed for the parent polyisobutylene, and therefore behaves as a higher molecular weight polymer. This behavior can be attributed to the aggregation of the oligo(β-alanine) segments in the chain ends. Because the FT-IR shows that the oligo(β-alanine) segment association is incomplete, it is reasonable to think that not enough chain ends are associating for the system to reach a gel point. So rather
than the oligo(β-alanine) domains acting as cross-linking points, they are acting as points of chain extension.

The crystalline structure of polymer 4c was examined by WAXD and compared to the known diffraction pattern of Nylon 3. It was found that the oligo(β-alanine) domain of polymer 4c has a very similar crystalline structure to that of Nylon 3. The comparison of the infrared spectrum of Nylon 3 with polymers 4b – 4d further confirms this.

The effect of the oligo(β-alanine) segment length on the properties of polymers 4b – 4d is surprising considering the difference between each polymer is only by a single repeat unit in oligo(β-alanine) segment. The T_m s show a strong dependence of oligo(β-alanine) segment length where trimer, tetramer and pentamer show T_m s of 100, 188, and 234 °C. The mechanical properties also show a similar trend where the longer peptides give a material with a higher modulus and higher ultimate strength.
CHAPTER II

BUTYL RUBBER PHYSICALLY CROSS LINKED BY OLIGO(β-ALANINE) PENDENT GROUPS

3.1 Introduction

This introduction will discuss the grafted copolymers with hydrogen bonding pendent groups. Similar work by the Stadler group and the Montès group are discussed below. The applicability of the ene reaction to chemically modifying butyl rubber is also discussed.

3.1.1 Grafted Copolymers with Hydrogen Bonding Pendent Groups

Grafted copolymer thermoplastic elastomers (TPE)s are typically elastomeric chains that are physically crosslinked by the interaction of associating pendent groups. To attain a high strength material, these pendent groups must form discrete hard domains that are immiscible with the soft backbone segment. The hard domains can then act not only as crosslinking points, but also as reinforcing domains. To achieve high strength, both the degree of crosslinking and the volume of reinforcing domains is very important. For covalently crosslinked elastomers, it is understood that as the crosslinking
density increases, the tensile strength passes through a maximum. Grafted copolymer thermoplastic elastomers allow for a simple adjustment of the physical crosslink density by adjusting the grafting density. The volume of reinforcing domains can be controlled independently of the grafting density by adjusting the hard segment length. An increase in the volume of reinforcing domains is known to increase the modulus of elastomers. However, if the volume of reinforcing domains is too high, the material will behave with more plastic character than elastic.

Stadler et al. examined the properties of polybutadiene grafted with 4-(3,5-di-oxo-1,2,4-triazolin-4-yl)benzoic acid (TZB). The structure of TZB (Figure 3.1) contains two hydrogen bonding sites; the carboxylic acid and the urazole. These two sites associate as urazole – urazole and acid – acid pairs to form an extended hydrogen bonded structure (Figure 3.2). The extended hydrogen bonded structures aggregate together to form a higher ordered bundle-like structure, which is phase separated from the polybutadiene segments (Figure 3.2).
Figure 3.1 (left) Molecular structure of TZB (right) hydrogen bonded structure of TZB.

Figure 3.2 a) The extended hydrogen bonded structure of TZB and b) the higher order aggregation of the extended hydrogen bonded structures.\textsuperscript{49}
The tensile properties of polybutadiene with a molecular weight of 400,000 g/mol and various mol percents of TZB are shown in Figure 3.3. The mol percent of TZB has a pronounced effect on the tensile properties of the system in that the modulus is shown to increase as the mol percent of TBZ increases. The samples with the higher percents also show more pronounced yielding. Figure 3.3 shows the cyclic stress-strain behavior for the sample with 4% TBZ. In this experiment, the strain was increased by one unit (with respect to original length) for each cycle. In the first cycle, the material shows a high Young’s modulus followed yielding. In each following cycle, Young’s modulus is decreased. This is an indication that some molecular structure is being broken when the sample is strained. To emphasize this point, a control experiment was done using polybutadiene grafted with non-associating groups that shows no strain-softening when cycled. The stress strain behavior observed for this grafted system is very similar to that observed for segmented block copolymers.³

The temperature dependence of the mechanical properties of the polybutadiene TZB system was examined with dynamic mechanical analysis (DMA). For this experiment, low molecular weight polybutadiene (31,000 g/mol) was grafted with TZB units at 0, 0.5, 1.0, 2.0, and 4 mol %. With no hard content, the polymer shows typical melt behavior. With the addition of TZB units, the material shows viscoelastic solid behavior. Increasing TZB content increases both the plateau modulus and the melting temperature. This trend is again similar to what is observed for segmented block copolymers.³
Figure 3.3 (left) Tensile test with a strain rate of 20 mm/min for various mol percents of hard content (right) a cyclic stress strain test performed at 20 mm/min with a sample containing 4 mol % hard content.\textsuperscript{49}

Figure 3.4 Storage modulus as a function of temperature at various mol percents of hard content. (□): 0\%, (●): 0.5\%, (△): 1\%, (○): 2\%, (▲): 4\%. The test was performed at a constant frequency of 0.14 rad/sec.\textsuperscript{49}
Stadler’s work demonstrates that grafted copolymer TPEs can have properties similar to those observed for segmented copolymers. Recently, Hélène Montès et al directly compared a grafted system to a triblock system. Polydimethysiloxane (PDMS) was used as the polymer backbone and bis-ureas for the associating groups. The bis-urea segments phase separate to form crystalline domains. The chemical structures are shown in Figure 3.5, and the molecular properties and tensile properties shown in Table 3.1. Both the end-functionalized and grafted polymers show crystalline bis-urea domains by SAXS and DSC. At room temperature the polymers show viscoelastic solid properties, when heated above the DSC determined melting temperatures, viscous liquids result.
Figure 3.5 Chemical structures of the Bis-urea hard segment (bottom right), grafted PDMS (left) and end-functionalized PDMS (top right).

Table 3.1 Molecular and Tensile Properties of Bis-Urea PDMS Copolymers

<table>
<thead>
<tr>
<th>Name</th>
<th>%N&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (g/mol)</th>
<th>Stress at Break (Mpa)</th>
<th>Strain at Break (%)</th>
<th>Youngs Modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuP/PDMS(4)/BuP</td>
<td>2.73</td>
<td>4500</td>
<td>too brittle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuP/PDMS(29)/BuP</td>
<td>0.43</td>
<td>25000</td>
<td>0.15 ± 0.05</td>
<td>25 ± 7</td>
<td>0.55</td>
</tr>
<tr>
<td>PDMS(13)-g-BuP</td>
<td>2.26</td>
<td>13000</td>
<td>0.35 ± 0.1</td>
<td>5 ± 2</td>
<td>5.5</td>
</tr>
<tr>
<td>PDMS(30)-g-BuP</td>
<td>2.76</td>
<td>31000</td>
<td>4.0 ± 0.1</td>
<td>280 ± 30</td>
<td>10.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Nitrogen content determined by elemental analysis, and proportional to the bis-urea content. <sup>b</sup>Determined by SEC. Reprinted with permission from Macromolecules. Copyright 2005 American Chemical Society.
The end-functionalized polymers represent two extremes. BuP/PDMS(4)/BuP has a low molecular weight PDMS block (4500 g/mol) and a high weight percent of bis-urea. The resulting material is a brittle solid that is so weak that it cannot be examined with tensile testing or rheology. This low strength can be attributed to the soft block molecular weight being too low to allow for any entanglements between hard blocks. At the other extreme is the end-functionalized polymer Bu/PDMS(29)/BuP, which has a high molecular weight middle block (25,000 g/mol) and lower weight percent of bis-urea. At 25,000 g/mol, the middle block is sufficiently entangled. However, high strength is not achieved. The resulting material is not brittle, but soft and weak. The low strength in this case is a result of the hard block content being too low to effectively reinforce the polymer. This comparison brings to light the challenge of using short hard blocks with a triblock architecture. When the soft block molecular weight is high enough for sufficient entanglement the percent of hard block is too low, or when the hard block content is high enough the soft block molecular weight is too low.

The two grafted copolymers have very similar weight percents of hard content, but differ in their total molecular weights. Polymer PDMS(13)-g-BuP has a low molecular weight of 10,500 g/mol. At this molecular weight this polymer is analogous to BuP/PDMS(4)/BuP in that the soft block molecular weight is too low for sufficient entanglement. The result is a weak material. The higher molecular weight BuP/PDMS(30)/BuP (31,000 g/mol) displays an ultimate strength, Young’s modulus, and ultimate strain that are much higher than the other
polymers. This is because the ability to independently adjust the hard block content and soft block molecular weight has been taken advantage of. BuP/PDMS(30)/BuP contains a high enough weight percent of hard block for efficient reinforcement to take place and a high enough molecular weight PDMS block for sufficient entanglement.

3.1.2 Modification of Butyl Rubber and the ene Reaction

The carbon-carbon double bonds in the isoprene units of butyl rubber can be used as reactive sites for the attachment of functional groups. Halogenation with chlorine or bromine provides reactive sites for nucleophiles such as alcohols or carboxylic acids. Maleic anhydride has also been reportedly attached to butyl rubber through a radical reaction. Polymers suitable for many applications can be produced in this way, but these reactions are limited by non-quantitative transformations. Gillies et al demonstrated a quantitative method to functionalize butyl rubber by transforming the isoprene units to exo-conjugated dienes, which are then reacted with substituted alkenes in a Diels-Alder cycloaddition.

The ene reaction is a chemical reaction between an enophile and an alkene with an allylic proton. Isoprene units have an allylic proton and require no transformations prior to reaction with a suitable enophile. Alkynes with electron withdrawing groups such as esters have been shown to be effective enophiles. Improved yields and shorter reaction times have been reported when the reaction is catalyzed by Lewis acids such as AlCl₃ and EtAlCl₃.
3.2 Project Concept

The block copolymers discussed in the previous chapter lay the foundation for a new class of thermoplastic elastomers that use oligo(β-alanine) as hard blocks. It was demonstrated that by end-functionalizing polyisobutylene with oligo(β-alanine) a thermoplastic elastomer was obtained. However, it did not possess the high strength typical of thermoplastic elastomers. In an attempt to solve this problem, a grafted copolymer molecular architecture has been adopted. The polymer backbone is high molecular weight polyisobutylene with 1.1 mol % of statistically distributed polyisoprene units, known as butyl rubber (BR). The unsaturation of the isoprene units will be exploited to graft monodisperse oligo(β-alanine) groups. The molecular architecture is shown in Figure 3.6a.

Based on what was learned from the telechelic oligo(β-alanine) polymers studied in Chapter 2, it is known that PIB and oligo(β-alanine) phase separate. The oligo(β-alanine) segments form long thin ribbon like crystalline domains dispersed in a rubber PIB matrix. It is reasonable to think a very similar morphology will be displayed with the grafting architecture (Figure 3.6d).
Figure 3.6 Schematic representation of grafted polymers a) the molecular structure where the green line is the soft butyl segment and the blue arrows represent the hard oligo(β-alanine) segment with Z monomers b) Butyl rubber grafted with oligo(β-alanine) and non-hydrogen bonding groups c) Butyl rubber grafted with oligo(β-alanine) pendant groups of two different sizes d) The envisioned morphology where the oligo(β-alanine) segments crystalize to form discrete domains dispersed in an amorphous rubbery domain of butyl rubber chains.
The grafting architecture allows for easy adjustment of several structural parameters. First, the length of the oligo(β-alanine) segments (z) can be adjusted. This will change both the weight percent of hard content and the size of the crystalline domains in the oligo(β-alanine) chain direction. Second, the average molecular weight between hard segments (M_H) can also be adjusted. This can be achieved by grafting both non-hydrogen bonding groups and oligo(β-alanine) to the butyl chain. Having the ability to adjust M_H allows z to be adjusted independently of hard segment weight percent. Section 3.6.3 will discuss this approach.

It is hypothesized that by having hard segments with multiple discrete lengths, self-sorting hard domains may result (Figure 3.6c). To test this, butyl rubber has been grafted with oligo(β-alanine) unimers and oligo(β-alanine) trimmers on the same chain. Section 3.6.4 discusses evidence for self-sorting, and the mechanical properties of butyl rubber grafted with oligo(β-alanine) segments of different lengths.

3.3 Experimental

The experimental section is broken into sections discussing the materials, instrumentation and synthesis.

3.3.1 Materials and Instrumentation

All solvents were purchased from Sigma-Aldrich and used as received. Chlorotrimethylsilane, benzyl alcohol, 4-methylmorpholine, 4-
dimethylaminopyridine, \(N,N\)-disuccinimidyl carbonate, \(\beta\)-alanine, di-\(t\)-butyl dicarbonate, 3-(ethyliminomethyleneamino)-\(N,N\)-dimethylpropan-1-amine-\(N,N'\)-dicyclohexylcarbodiimide, and 4M HCl dioxane solution were purchased from Oakwood. Pd/C, triethylamine, perfluorophenol, 4-nitrophenol, propiolic acid, methyl propiolate, EtAlCl\(_3\) and triphenyl phosphene were purchased from Sigma-Aldrich. Triethylamine was dried over CaH\(_2\) and distilled prior to use. All other reagents were used as received. The butyl rubber was produced by Exxon and provide as a gift from The Goodyear Tire and Rubber Company. The oligo(\(\beta\)-alanine)s (11a – 11d) were synthesized following a solution-phase peptide coupling procedure previously described in the literature.

Chemical structures were characterized with nuclear magnetic resonance (NMR) spectroscopic methods. The spectra were acquired on either a Varian Mercury 300-MHz or a Varian Avance 500 MHz instrument. Chemical shifts were determined using solvent peaks as the references.

Gel permeation chromatography (GPC) was performed at 30 °C using three tandem Waters HR styragel columns and THF as the solvent. The eluents were monitored using an inline Wyatt Dawn EOS multiangle laser light scattering (MALLS) detector and a Waters Model 2414 differential refractometer concentration detector.

Fourier transform infrared (FT-IR) spectroscopy was performed on a Digilab Excalibur FTS 3000 series FT-IR spectrometer with Win-IR Pro Software. All FT-IR spectra were collected at a resolution of 4 cm\(^{-1}\). All samples were prepared by casting onto NaCl plates from a CHCl\(_3\) solution.
Differential Scanning Calorimetry (DSC) experiments were performed on a TA instrument model Q2000 with Advantage software version 2.8.0.382. Samples between 10.00 and 18.00 mg were loaded in aluminum pans. Experiments were performed under a nitrogen atmosphere and a temperature ramp rate of 10 °C/min was used. All samples were annealed prior to analysis according to the procedure described below.

TGA analysis was performed on a TA instrument (model Q500). Analysis was performed under both air and nitrogen atmospheres and samples were heated at a ramp rate of 10 °C/min.

For mechanical and rheological testing, all samples were hot-pressed into a 1 mm thick mold under nitrogen protection. Each sample was heated to 20 °C above its respective melting temperature under pressure (5,000 lb). The temperature was then slowly reduced to the melting temperature and held for ten minutes at high pressure (15,000 lb). The sample was then cooled slowly to 10 °C below the melting temperature and held for an additional ten minutes. The press was then slowly cooled before removing the polymer and mold. DMA tests were performed on an RSA 3 dynamic mechanical analyzer. Frequency sweep tests were performed at 30 °C. The clamp distance was set at 5 mm and samples were deformed to a strain of 2 % unless otherwise specified. DMA temperature sweep tests were performed under a nitrogen atmosphere at clamp distance of 5 mm, a frequency of 1 Hz, a strain of 2 % unless specified otherwise, and a temperature ramp rate of 5 °C/min was used.
Tensile tests were performed on the films mentioned above by first dieing out the sample with an ASTM D638 Type V dog bone die. Tensile tests were performed at ambient temperature at a strain rate of 50 mm/min until failure. Samples were loaded with a 40 mm gap distance and strain gauges were used to measure the strain. The strain gauges were set at a initial distance of 10 mm. Cyclic loading was performed on the same dog bone samples at a clamp distance of 40 mm and a speed of 50 mm/min and cycled to a max extension of 150 mm. Strain for these experiments was not measured with the strain gauge, but rather calculated from clamp displacement divided by the initial gap ($\epsilon/\epsilon_0$).

3.3.2 Synthesis

*Perfluorophenyl propiolate [8a]*

A flask was charged with pentafluorophenol (10.95 g, 59.49 mmol) and purged with nitrogen. Ethyl acetate (120 mL) and propiolic acid (3.60 mL, 59.49 mmol) were added to the flask. The solution was chilled to 0 °C. A separate solution of DCC (13.50 g, 65.43 mmol) in ethyl acetate (80 mL) was chilled under nitrogen atmosphere. The DCC solution was slowly added to the propiolic acid solution. The solution was stirred at 0 °C for 4 hours, and then removed from the cold bath and stirred at room temperature over night. The resulting slurry was filtered to remove the insoluble DCU. The solution was then concentrated and recrystallized from ethyl acetate at 0 °C to produce brown crystals (4.3 g, 33%).

$^1$H NMR (400 MHz; CDCl₃): $\delta$ 3.23 (s, 1H). $^{19}$F NMR (300 MHz; CDCl₃): $\delta$ -155.0 (d, $J = 19.5$ Hz, 2H), -159.5 (t, $J = 23.5$, 1H), -164.6 (t, $J = 23.0$ 2H) ppm.
**4-Nitrophenyl propiolate [8b]**

A flask was charged with 4-nitrophenol (10.0 g, 71.8 mmol) and purged with nitrogen. Ethyl acetate (120 mL) and propiolic acid (4.46 mL, 71.8 mmol) were added to the flask, and the solution was chilled to 0 °C. A separate solution of DCC (16.31 g, 79.07 mmol) in ethyl acetate (80 mL) was chilled under nitrogen atmosphere. The DCC solution was slowly added to the propiolic acid solution, and the solution stirred at 0 °C for 4 hours. The solution was then allowed to warm to room temperature and stirred overnight. The resulting suspension was filtered to remove DCU, and the solvent evaporated *in vacuo*. The product was then recrystallized from a 3:1 chloroform and hexane solution at 0 °C to produce white crystals. The crystals were collected by vacuum filtration and dried *in vacuo* (7.60 g, 55%). $^1$H NMR (300 MHz; CDCl$_3$): $\delta$ 8.27 (d, $J$ = 9.1 Hz, 2H), 7.34 (d, $J$ = 9.1 Hz, 2H), 3.16 (s, 1H) ppm. $^{13}$C ($^1$H) NMR (126 MHz; CDCl$_3$): $\delta$ 154.2, 149.6, 145.9, 125.4, 122.2, 78.0, 73.6 ppm.

**2,5-Dioxopyrrolidin-1-yl propiolate [8d]**

A flask was charged with N-hydroxysuccinimide (5.0 g, 43.44 mmol) and purged with nitrogen. Ethyl acetate (60 mL) and propiolic acid (2.23 mL, 35.9 mmol) were added to the flask and chilled to 0 °C. A separate solution of DCC (8.15 g, 39.5 mmol) in ethyl acetate (40 mL) was chilled under nitrogen. The solution was stirred at 0 °C for 4 hours, and then removed from the cold bath and stirred at room temperature over night. The resulting slurry was filtered to remove the insoluble DCU. The solution was then concentrated and recrystallized from...
ethyl acetate at 0 °C to give white crystals that were filtered out and dried under vacuum. (4.42g, 68%) $^1$H NMR (300 MHz; CDCl$_3$): δ 3.29 (s, 1H), 2.84 (s, 4H) ppm.

*Perfluorophenyl propiolate ester grafted butyl rubber [9a]*

Butyl rubber (100 g, 26.31 mmol isoprene units) was first dissolved in anhydrous benzene (1000 mL). Ester 8a (12.43 g, 52.63 mmol) was then added as a solid and quickly dissolved. A 1.8 M stock solution of EtAlCl$_2$ in toluene (14.61 mL, 26.31 mmol) was added dropwise to the solution in three separate charges. The reaction stirred for one hour and was then precipitated into MeOH stirred with a mechanical stirrer. Residual solvent was removed under reduced pressure (111 g, 99%). $^1$H NMR, $^{19}$F NMR and FT-IR are shown in Figures 3.7, 3.8, and 3.9 respectively. $M_n$: 449 x $10^3$ g/mol, $M_w/M_n$: 1.4
Figure 3.7 $^1$H NMR spectrum of 9a in CDCl$_3$

Figure 3.8 $^{19}$F NMR spectrum of 9a in CDCl$_3$ referenced to C$_6$F$_6$
Figure 3.9 FT-IR of 9a cast on a salt plate from CDCl₃. (1767 cm⁻¹ C=O stretch, 1641 cm⁻¹ C=C stretch in aromatic rings, 1521 cm⁻¹ aromatic ring stretch, 1003 cm⁻¹ C-F deformations)
4-Nitrophenol propiolate ester grafted butyl rubber [9b]

Butyl rubber (5.0 g, 1.31 mmol C=C) was dissolved in anhydrous benzene (50 mL). 8b was added (6.57 mmol) and stirred until a homogenous solution was achieved. AlCl₃ (0.172 g, 1.32 mmol) was added, and the solution was stirred for 15 hr. The polymer was then isolated by precipitation in MeOH and dried under vacuum. (4.9 g, 98%) $^1$H NMR and FT-IR spectra are shown in Figures 3.10 and 3.11. $M_n$: $231 \times 10^3$ g/mol, $M_w/M_n$: 1.5
Figure 3.10 $^1$H NMR spectrum of 9b in CDCl$_3$

Figure 3.11 FT-IR spectrum of 9b cast on a salt plate from CDCl$_3$ (1748 cm$^{-1}$, C=O stretch; 1643, 1614, and 1593 cm$^{-1}$, C=C stretch in aromatic rings; 1530 cm$^{-1}$, anti-symmetrical NO$_2$ stretch; 1346 cm$^{-1}$, symmetrical NO$_2$ stretch).
**Methyl ester grafted butyl rubber [9c]**

Using 8c as the propiolic ester, the same procedure for 9b was used to make 9c (4.8 g, 96%) ^H is shown in Figure 3.12.

**Hydrogenation of 9a using Wilkinson’s catalyst [10a]**

An autoclave was charged with 9a (5 g, 2.1 mmol C=C), RhCl(PPh₃)₃ (0.04 g, 0.04 mmol), triphenylphosphine (0.1 g, 0.42 m mol) and hexane (200 mL) in a glove box. After the polymer was dissolved, the autoclave was charged with hydrogen (700 psi) and heated to 100 °C for 48 hours. The polymer was isolated by precipitation in methanol and dried under vacuum (4.9 g, 98%) ^H NMR shown in 3.13. \( M_n; 449 \times 10^3 \) g/mol, \( M_w/M_n; 1.4 \)
Figure 3.12 $^1$H NMR spectrum of 9c in CDCl$_3$

Figure 3.13 $^1$H NMR spectrum of 10a in CDCl$_3$
Oligo(β-alanine) grafted butyl rubber, hydrogenated [12a – 12c]

The procedures for the grafting of oligomers 11a – 11c to polymer 10a are the same. Below the procedure for 12a is provided as an example.

A solution of 10a (5.0 g, 1.04 mmol ester) and 11a (0.23 g, 1.25 mmol) was prepared in anhydrous chloroform (50 mL) and anhydrous DMSO (5 mL) at room temperature under the protection of nitrogen. Et$_3$N (0.73 mL, 5.20 mmol) was added and the solution refluxed for 24 hours. The polymer was then isolated by precipitation in MeOH and dried under vacuum (4.8 g, 96%) $^1$H NMR shown in Figure 3.14 and FT-IR in 3.15.

The synthesis of polymer 12b yielded 98% product. The $^1$H NMR and FT-IR for 12b are shown in Figures 3.16 and 3.17. The synthesis of polymer 12c yielded 96% product. The $^1$H NMR and FT-IR for 12c are shown in Figures 3.18 and 3.19.
Figure 3.14 $^1$H NMR spectrum of 12a in CDCl$_3$

Figure 3.15 FT-IR spectrum of 12a cast on a salt plate from CDCl$_3$ (3283 cm$^{-1}$, N-H stretch amide A; 1639 cm$^{-1}$, C=O stretch amide I; 1553 cm$^{-1}$, N-H in-plane waggle amide II)
Figure 3.16 $^1$H NMR spectrum of 12b in CDCl$_3$.

Figure 3.17 FT-IR spectrum of 12b cast on a salt plate from CDCl$_3$ (see Figure 3.15 for assignment).
Figure 3.18 \[^{1}\text{H} \text{NMR} \] spectrum of 12c in CDCl\(_3\) and TFA-d

Figure 3.19 FT-IR spectrum of 12c cast on a salt plate from CDCl\(_3\) (see Figure 3.15 for assignment).
**Oligo(β-alanine) unsaturated grafted butyl rubber [13a, 13b]**

The procedures for the grafting of oligomers 11b and 11c to polymer 9a are the same. The procedure for 13a is provided below as an example.

The ester grafted butyl rubber, 9a (1 g, 0.21 mmol ester) was dissolved in anhydrous CHCl₃ (10 mL). Next, compound 11b (0.067 g, 0.26 mmol) was added followed by Et₃N (0.18 ml, 1.31 mmol). The solution was then set to reflux under a nitrogen atmosphere for 24 hours. The polymer was then isolated by precipitation into methanol and dried under vacuum. (0.97 g, 97%) ¹H NMR shown in Figure 3.20 FT-IR spectrum shown in Figure 3.21.

Polymer 13b yielded 98% product. The ¹H NMR of 13b is shown in Figure 3.22 in CDCl₃ and TFA-d and the FT-IR in Figure 3.23.
Figure 3.20 $^1$H NMR spectrum of 13a in CDCl$_3$.

Figure 3.21 FT-IR spectrum of 13a cast from CDCl$_3$ onto a salt plate (see Figure 3.15 for assignment).
Figure 3.22 $^1$H NMR spectrum of 13b in CDCl$_3$ and TFA-d.

Figure 3.23 FT-IR spectrum of 13b cast on a salt plate from CDCl$_3$ (see Figure 3.15 for assignment).
Piperidine grafted butyl rubber [14a]

Polymer 9a (1 g, 0.21 mmol) was dissolved in anhydrous CHCl₃ (10 mL). Next, piperidine (0.052 mL, 0.52 mmol) was added and the solution stirred at room temperature for 24 hours. The polymer was isolated by precipitation into methanol and dried under vacuum (0.98 g, 98%). ¹H NMR is shown in Figure 3.24, COSY is NMR shown in Figure 3.25, and FT-IR spectrum shown in Figure 3.26.

Scheme 3.1 Synthetic route for mixed grafted polymers of oligo(β-alanine) and piperidine.
Figure 3.24 $^1H$ NMR spectrum of 14a in CDCl$_3$.

Figure 3.25 COSY NMR spectrum of 14a in CDCl$_3$. 

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Figure 3.26 FT-IR spectrum of 14a cast on a salt plate from CDCl$_3$. 
Butyl rubber with grafted with β-alanine dimer and piperidine [14b and 14c]

The procedures for the mixed grafting of 9a with 11b and piperidine at ratios of 7:1 and 1:4 are the same. As an example, the procedure for 14b is given below.

Polymer 9a (1 g, 0.21 mmol), was dissolved in anhydrous CHCl₃ (10 mL). Next, 11b (0.039 g, 0.015 mmol) was added followed by Et₃N (0.11 ml, 0.7 mmol). The solution was stirred under a nitrogen atmosphere for 24 hours at room temperature. Piperidine (0.010 mL, 0.10 mmol) was then added and the solution stirred at room temperature for an additional 24 hours. The polymer was isolated by precipitation into methanol and dried under vacuum (0.99 g, 99%). ¹H NMR is shown in Figure 3.27, and FT-IR spectrum shown in Figure 3.28.

The procedure for polymer 14c yielded 97% product. The ¹H NMR is shown in Figure 3.29, and the FT-IR spectrum shown in Figure 3.30.
Figure 3.27 $^1$H NMR spectrum of 14b in CDCl$_3$.

Figure 3.28 FT-IR spectrum of 14b cast on a salt plate from CDCl$_3$ (see Figure 3.15 for assignment).
Figure 3.29 $^1$H NMR spectrum of **14c** in CDCl$_3$.

Figure 3.30 FT-IR spectrum of **14c** cast on a salt plate from CDCl$_3$ (see Figures 3.15 and 3.26 for assignment).
Butyl rubber with mix grafting of oligo(β-alanine) unimer and oligo(β-alanine) trimer at a ratio of 1:10 [12d]

Polymer 10a (5 g, 1.04 mmol) and oligomer 11c (0.033 g, 0.104 mmol) were dissolved in anhydrous chloroform (50 mL) and DMSO (5 mL). Et₃N (0.74 mL, 5.20 mmol) was added and the solution refluxed for 6 hours. 11a (0.187 g, 1.04 mmol) was added and the solution refluxed for an additional 24 hours. The polymer was then isolated by precipitation in methanol and dried under vacuum (0.99 g, 99%). ¹H NMR shown in Figure 3.31 FT-IR spectrum shown in Figure 3.32.

Scheme 3.2 Synthetic route for mixed grafted polymers with oligo(β-alanine)s of different lengths
Figure 3.31 $^1$H NMR spectra of 12d in CDCl$_3$ and TFA-d.

Figure 3.32 FT-IR of 12d cast from CDCl$_3$ (see Figure 3.15 for assignment).
Butyl rubber with mix grafting of oligo(β-alanine) unimer and oligo(β-alanine) trimer at a ratio of 1:1 [12e]

Polymer 10a (5g, 1.04 mmol), compound 11c (0.20 g, 0.06 mmol), and compound 11a (0.11 g, 0.06 mmol) were dissolved in anhydrous chloroform (50 mL) and DMSO (5 mL). Et$_3$N (0.74 mL, 5.20 mmol) was added and the solution set to reflux for 24 hours. The polymer was then isolated by precipitation in methanol and dried under vacuum (0.99 g, 99%). $^1$H NMR shown in Figure 3.33 FT-IR spectrum shown in Figure 3.34.
Figure 3.33 $^1$H NMR spectrum of 12e in CDCl$_3$ and TFA-d.

Figure 3.34 FT-IR of 12e cast from CDCl$_3$.
3.4 Results

The results section discusses the synthesis and characterization of grafted butyl rubber. Interpretation of the data is reserved for the discussion section.

3.4.1 Synthesis

Four propiolate esters, $8a - 8d$, were synthesized by DCC coupling of propiolic acid to the appropriate alcohol (Scheme 3.3). Among them, $8a - 8c$ were successfully grafted to butyl rubber through a Lewis acid-catalyzed ene reaction with the isoprene units, but $8d$ was unreactive toward butyl rubber under the conditions examined here. The effect of ene reaction conditions on backbone molecular weight was examined for the reaction of $8a$ and $8b$ with butyl rubber (Table 3.2).

Hydrogenation of $9a$ by Wilkinson’s catalyst was carried out to remove any unsaturation in the butyl rubber backbone. This was done to avoid unwanted side reactions of the unsaturated bonds during high temperature processing of the final polymers.

$\beta$-Alanine oligomers, $11a - 11c$, were synthesized by solution phase coupling techniques similar to what was discussed in Chapter 2. The oligo($\beta$-alanine)s were coupled to $9a$ and $10a$ to give oligo($\beta$-alanine) grafted copolymers $12a - 12c$, $13a$ and $13b$. Mechanical stirring was required to break up oligo($\beta$-alanine) association and ensure a complete reaction. Alternatively, the addition of DMSO (10 vol%) was found to break up aggregation. Polymer $9a$ was also, grafted with the secondary amine, piperidine, to produce $14a$. 
Butyl rubber with mixed grafts of different oligo(β-alanine) lengths were synthesized. Oligo(β-alanine)s 11a and 11b were grafted to 9a at ratios of 10:1 and 1:1 to give polymers 12e and 12d, respectively. Butyl rubber with mixed grafts of oligo(β-alanine) and piperidine were also synthesized. 9a was grafted with piperidine and 12c at ratios of 1:4 and 7:1 to produce polymers 14b and 14c.
Scheme 3.3 The synthetic route established to graft oligo(β-alanine) units to butyl rubber.
<table>
<thead>
<tr>
<th>Trial</th>
<th>Isoprene Equivalents</th>
<th>Ester Equivalents</th>
<th>EtAlCl3 Equivalents</th>
<th>AlCl3 Equivalents</th>
<th>Reaction Time (Hr)</th>
<th>Mn</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8b</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>1</td>
<td>66</td>
<td>247,000</td>
</tr>
<tr>
<td>2</td>
<td>8b</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>1</td>
<td>18</td>
<td>231,500</td>
</tr>
<tr>
<td>3</td>
<td>8b</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>24</td>
<td>43,300</td>
</tr>
<tr>
<td>4</td>
<td>8b</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>24</td>
<td>75,570</td>
</tr>
<tr>
<td>5</td>
<td>8b</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>0.5</td>
<td>48</td>
<td>108,400</td>
</tr>
<tr>
<td>6</td>
<td>8a</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>3</td>
<td>343,000</td>
</tr>
<tr>
<td>7</td>
<td>8a</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>449,400</td>
</tr>
</tbody>
</table>

Table 3.2 Resulting Molecular Weights after the Ene Reaction
Table 3.3 Molecular Structure Information for Grafted Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(^a^\text{Butyl } M_n) (g/mol)</th>
<th>(^a^\text{Butyl} M_w/M_n)</th>
<th>(z)</th>
<th>\text{Oligo(β-alanine) Content (wt %)}</th>
<th>(^b^M_H) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>449,000</td>
<td>1.4</td>
<td>1</td>
<td>3.0%</td>
<td>4,627</td>
</tr>
<tr>
<td>12b</td>
<td>449,000</td>
<td>1.4</td>
<td>2</td>
<td>4.4%</td>
<td>4,620</td>
</tr>
<tr>
<td>12c</td>
<td>449,000</td>
<td>1.4</td>
<td>3</td>
<td>5.8%</td>
<td>4,669</td>
</tr>
<tr>
<td>13a</td>
<td>449,000</td>
<td>1.4</td>
<td>2</td>
<td>4.4%</td>
<td>5,516</td>
</tr>
<tr>
<td>13b</td>
<td>449,000</td>
<td>1.4</td>
<td>3</td>
<td>5.8%</td>
<td>4,886</td>
</tr>
<tr>
<td>14a</td>
<td>449,000</td>
<td>1.4</td>
<td></td>
<td>0.0%</td>
<td>-</td>
</tr>
<tr>
<td>14b</td>
<td>449,000</td>
<td>1.4</td>
<td>2</td>
<td>0.6%</td>
<td>36,120</td>
</tr>
<tr>
<td>14c</td>
<td>449,000</td>
<td>1.4</td>
<td>2</td>
<td>4.5%</td>
<td>6,083</td>
</tr>
<tr>
<td>12d</td>
<td>449,000</td>
<td>1.4</td>
<td>1, 3 (10:1)</td>
<td>3.2%</td>
<td>4,980</td>
</tr>
<tr>
<td>12e</td>
<td>449,000</td>
<td>1.4</td>
<td>1, 3 (1:1)</td>
<td>4.4%</td>
<td>4,870</td>
</tr>
</tbody>
</table>

\(^a^\text{determined from GPC} \hspace{1cm} ^b^\text{M}_H\) is the molecular weight between grafted oligo(β-alanine) units determined from \(^1^H\) NMR.
3.4.2 FTIR

The solid state FTIR spectra of polymers 12a – 12e show the amide A, amide I, and amide II absorbance bands at 3287, 1641, and 1553 cm\(^{-1}\) respectively (Figure 3.35). These bands are characteristic of hydrogen bonded β-alanine groups. Polymers 13a and 13b show identical amide A, amide I and amide II bands to 12a – 12e. Polymer 14a shows no absorbance bands associated with hydrogen bonding. Polymer 14b shows the an amide A band and amide II band indicative of hydrogen bonded oligo(β-alanine). The amide I band is overlapped with the C=O absorbance band of the piperidine amide and cannot be observed. Polymer 14c shows amide A, amide I and amide II bands that are indicative of hydrogen bonded oligo(β-alanine) (Figure 3.36).
Figure 3.35 FT-IR spectrum of 12a (green), 12b (red), 12c (blue), 12d (purple) and 12e (maroon).

Figure 3.36 FT-IR spectrum (from top to bottom) 14c, 14b, and 14a.
3.4.3 Thermogravometric Analysis

All polymer samples were subjected to TGA analysis in air and nitrogen atmospheres as summarized in Table 3.4. The TGA curves in nitrogen for 12a – 12c are shown in Figure 3.37. All three curves show a major decomposition at about 370 °C, and a less pronounced step at slightly lower temperatures (~320 °C). The major decomposition occurs at almost the same temperature as the unfunctionalized butyl rubber. It can be attributed to the backbone decomposition. The decomposition at lower temperature is attributable to the oligo(β-alanine) segment decomposition.
Table 3.4 DSC and TGA Data for Grafted Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_m$</th>
<th>$T_g$</th>
<th>$^aT_{d99}$</th>
<th>$^bT_d$</th>
<th>$T_{d99}$</th>
<th>$T_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>96.8</td>
<td>-63.3</td>
<td>246</td>
<td>348</td>
<td>305</td>
<td>369</td>
</tr>
<tr>
<td>12b</td>
<td>136.9</td>
<td>-62.8</td>
<td>240</td>
<td>322</td>
<td>286</td>
<td>369</td>
</tr>
<tr>
<td>12c</td>
<td>173.5, 191.9</td>
<td>-64.5</td>
<td>256</td>
<td>338</td>
<td>286</td>
<td>367</td>
</tr>
<tr>
<td>14a</td>
<td>-</td>
<td>-62.3</td>
<td>243</td>
<td>358</td>
<td>278</td>
<td>366</td>
</tr>
<tr>
<td>14b</td>
<td>-</td>
<td>-63.4</td>
<td>276</td>
<td>350</td>
<td>308</td>
<td>366</td>
</tr>
<tr>
<td>14c</td>
<td>138.7</td>
<td>-62.6</td>
<td>284</td>
<td>356</td>
<td>298</td>
<td>365</td>
</tr>
<tr>
<td>12d</td>
<td>92.2</td>
<td>-64.6</td>
<td>247</td>
<td>332</td>
<td>302</td>
<td>369</td>
</tr>
<tr>
<td>12e</td>
<td>57.8</td>
<td>-64.0</td>
<td>269</td>
<td>367</td>
<td>297</td>
<td>371</td>
</tr>
<tr>
<td>13a</td>
<td>143.3, 192.9</td>
<td>-63.7</td>
<td>250</td>
<td>324</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13b</td>
<td>178.1</td>
<td>-63.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl</td>
<td>-</td>
<td>-65.4</td>
<td>265</td>
<td>332</td>
<td>304</td>
<td>363</td>
</tr>
</tbody>
</table>

$^a$Temperature at 1% decomposition  $^b$Major decomposition temperature

Figure 3.37 TGA curves of 12a, 12b, and 12c under nitrogen.
3.4.4 Differential Scanning Calorimetry

All samples were annealed prior to analysis by DSC and show a low temperature glass transition temperatures (T_g) (below -60 °C) characteristic of the polyisobutylene backbone. Polymers 12a – 12e, 13a, 13b and 14c show higher temperature transitions (above 90 °C) which are attributable to the melting and crystallization of the oligo(β-alanine) domains when heated and cooled respectively. 12c and 13b show two closely spaced T_m's that can be attributed to two kinds of oligo(β-alanine) trimer crystals. 14a and 14b show no high temperature transitions. 12e shows two melting endotherms (57.8 and 156.7 °C) and two crystallization temperatures (51.9 and 131.5 °C) that can be attributed to oligo(β-alanine) unimer and trimer domains. 12d shows no T_m or T_c attributable to the oligo(β-alanine) trimer. This is most likely due to the low weight percent of oligo(β-alanine) trimer grafts (0.5 wt%) in 12d.
Figure 3.38 DSC traces of a) 12a, b) 12b, c) 12c, d) 13a, and e) 13b.
Figure 3.39 DSC traces of a) 14a, b) 14b, and c) 14c.
Figure 3.40 DSC curves of a) 12d, b) 12e c) 12e, heating expanded, and d) 12e cooling expanded.
3.4.5 Mechanical Properties

To prepare the polymers for mechanical testing, all samples were hot pressed under nitrogen protection into a mold and died out into the appropriate test specimen as described in Section 3.3.1. For DMA analysis, the specimens were cut into thin strips (20 mm x 6 mm x 1 mm) and tensile testing, the specimens were died out using an ASTM D638 Type V die.

3.4.5.1 Dynamic Mechanical Analysis

DMA temperature sweeps were performed at a fixed frequency (1Hz) and strain amplitude (2%). 12a – 12c, and 13a show viscoelastic solid behavior from low temperatures (~0 °C) up to each polymer’s respective Tm, where E’ and E‖ drop (Figure 3.41). The melt transitions are reversible as demonstrated by the cycled heating and cooling of 13a (Figure 3.41d). The melt transition of 13a shows a dependency on the strain amplitude as demonstrated on in Figure 3.42. 12d and 12e show two transitions attributable to the melting of oligo(β-alanine) unimers (low temperature transitions) and oligo(β-alanine) trimers (high temperature transitions) (Figure 3.43). 13b (not shown) shows nearly the same behavior as 12c.
Figure 3.41 DMA temperature ramp experiments of a) 12a, b) 12b, c) 12c, and d) 13a.

Figure 3.42 DMA temperature sweep for 13a at 2 % strain, 8 % strain, and 12 % strain.
Figure 3.43 Temperature ramp DMA test of a) 12d and b) 12e
3.4.5.2 Stress Strain Properties

Samples were pulled in uniaxial tension at a strain rate of 50 mm/min until failure. Figure 3.4 and Table 3.5 shows the tensile properties of 12a – 12e, and the butyl rubber homopolymer. 12a – 12e show high initial moduli followed by yielding and elongation up to about 800% where all samples show an upturn in stress.
Figure 3.44 Tensile test of (from top to bottom) 12c, 12b, 12e, 12a, 12d, and butyl homopolymer
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Set(^a) (%</th>
<th>Hysteresis(^b) (%)</th>
<th>Toughness (KJ/m³)</th>
<th>(E_{10%}) (MPa)</th>
<th>(E_{100%}) (MPa)</th>
<th>(\gamma_b) (%)</th>
<th>(\sigma_b) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>29%</td>
<td>59%</td>
<td>12 ± 2</td>
<td>2.8 ± 0.1</td>
<td>0.66 ± 0.03</td>
<td>9740 ± 80</td>
<td>4.8 ± 0.6</td>
</tr>
<tr>
<td>12b</td>
<td>43%</td>
<td>64%</td>
<td>47 ± 6</td>
<td>6.8 ± 0.3</td>
<td>1.5 ± 0.1</td>
<td>1050 ± 20</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>12c</td>
<td>62%</td>
<td>72%</td>
<td>83 ± 6</td>
<td>16 ± 2.0</td>
<td>3.4 ± 0.2</td>
<td>1020 ± 80</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>12d</td>
<td>29%</td>
<td>54%</td>
<td>17 ± 1</td>
<td>2.9 ± 0.3</td>
<td>0.59 ± 0.01</td>
<td>1210 ± 10</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>12e</td>
<td>29%</td>
<td>60%</td>
<td>45 ± 4</td>
<td>5.5 ± 1.0</td>
<td>1.4 ± 0.1</td>
<td>1080 ± 30</td>
<td>15 ± 1</td>
</tr>
</tbody>
</table>

\(^a\) Measured after a 40 mm sample was deformed to 150 mm as discussed in Section 3.3. Stress strain data taken as an average of three specimen
3.4.5.3 Hysteresis and Set

Dog bone specimen were clamped at a gap of 40 mm and deformed at a rate of 50 mm/min up to a gap of 150 mm and then returned back to 40 mm. The tensile set was measured at the start of a second cycle as the point when stress goes above zero. Figure 3.45 shows hysteresis loops for polymers 12a, 12b, and 12c. The specimen with longer hard segments show higher hysteresis and tensile set as summarized in Table 3.5. Figure 3.46 shows the hysteresis loops for 12e and 12d.
Figure 3.45 Hysteresis loops of 12a, 12b, and 12c

Figure 3.46 Hysteresis loops for 12d, and 12e
3.5 Discussion

In the discussion section, the synthesis of polymers 12a – 12d, 13a, 13b, and 14a -14c are discussed first. The discussion is then broken into sections based on the fully grafted polymers 12a – 12c, the piperidine mixed grafted polymers 14a – 14c, and the grafted polymers with mixed oligo(β-alanine) lengths, 12d, and 12e, and a discussion of melting temperatures.

3.5.1 Synthesis

The synthesis section is broken into sections discussing the ene reaction, the amidation reaction, hydrogenation, and the synthesis of the mixed grafted polymers.

3.5.1.1 The ene Reaction and Amidation

To be a useful grafted intermediate, the propiolic ester must be readily grafted to butyl rubber through a Lewis acid catalyzed ene reaction and in a second step, coupled with oligo(β-alanine) in a condensation reaction. In the presence of AlCl₃ or EtAlCl₃, propiolic esters 8a – 8c readily undergo the ene reaction with the isoprene units in butyl rubber. 8d, however, did not react. 9a and 9b were successfully transformed to amides by both piperidine and the oligo(β-alanine)s. 9c, however, showed very poor reactivity toward oligo(β-alanine).

Although the anticipated transformation occurred, a decrease in polymer molecular weight was observed under some ene reaction conditions. If AlCl₃ was
added to the polymer solution in the absence of the ester, catastrophic chain
scission occurred. A rapid decrease in solution viscosity upon addition of the acid
was observed. Lewis acids are known to react with isoprene unit causing chain
scission in butyl rubber. When the ester was dissolved first, chain scission was
suppressed but still occurred. Ratios of esters and acids, and reaction times were
examined as shown in Table 3.2. The reaction between 9a and the less acidic
Lewis acid, EtAlCl₃, gave the highest molecular weight. The preferred method is
to use 8a to produce 9a.

3.5.1.2 Hydrogenation

Hydrogenation of the double bounds in 9a became necessary because
during polymer processing at high temperature, cross-linking occurred to
polymers 13a – 13b, which were synthesized initially. For this reason, the tensile
properties of 13a – 13b are not discussed in this thesis, but the spectroscopic
and thermal characterizations remain valid. The films of 12a – 13e could be
recycled several times with no changes in mechanical properties.

3.5.1.3 Mixed Grafting

Polymer 12d which contains a 10:1 mole ratio of grafted β-alanine unimer
and trimer was synthesized in a one-pot two-step process (Scheme 3.3). The
minor component 11c was added first and allowed to react. The progress of the
reaction was monitored with ¹⁹F NMR as shown in Figure 3.47. Disappearance of
the peaks due to starting material and appearance of the peaks due to the

134
products are clearly observable. The reaction was said to be complete when the ratio of starting ester to condensed phenol was 1:10. At this point the unimer 11a, was added in excess. The same method was used for 14b and 14c. Oligo(β-alanine) was added first followed by piperidine in the second step. Polymer 12e was prepared by a one-pot, one-step method where an equal ratio of 11a and 11c were added in slight excess to the polymer 10a. The ratio of grafted 11a and 11c is approximately the same as anticipated from the feed ratio of 11a and 11c.
Figure 3.47 $^{19}$F NMR spectrum of the crude reaction mixture for 12d.
3.5.2 Fully Grafted Polymers with one Length of Oligo(β-alanine) Hard Segment

The DSC thermographs in Figure 3.38 confirm that 12a – 12c, 13a and 13b are microphase separated into amorphous and crystalline domains. As a result of an increased number of hydrogen bonds, the Tm,s increase with oligo(β-alanine) segment length. To understand the secondary structure of these crystalline domains, they can be compared to the crystalline structure found in the end-functionalized polymer, 4c, in Chapter 2. The secondary structure of 4c was determined by comparison with the known structure of Nylon 3 by WAXD and FTIR spectroscopy. A comparison of the FT-IR spectra of polymers 12a – 12c shows the amide A, amide I, and amide II bands align well with 4c (Figure 3.48). Therefore the secondary structure of the oligo(β-alanine) domains in 12a – 12c are very similar to the secondary structure found in Nylon 3. The same can also be said for 13a and 13b.

It should also be noted that 12a, which has only one repeat unit of β-alanine, is fully hydrogen bonded. This is interesting because the end-functionalized polymer 4a contains two repeat units, but is not fully hydrogen bonded. This difference is possibly caused by the structural differences at the N and C termini of the molecules as shown in Figure 3.49. The 4a hard segments have bulkier terminal groups that may interfere with hydrogen bonding.
Figure 3.48 FT-IR spectrum of 4c (orange), 12a (green), 12b (red), and 12c (blue).

Figure 3.49 Structures of hard blocks in 12a (left) and 4c (right).
The melting temperatures determined by DMA (T_{m_{DMA}}) show the same trend that was observed as the DSC determined melting temperatures (T_{m_{DSC}}) where the longer oligo(β-alanine) segments have higher melting temperatures. The T_{m_{DMA}} for 12c corresponds well with the onset of melting observed by DSC. However, the T_{m_{DMA}}s for 12a, 13a, and 12b are approximately 70 °C lower than their respective T_{m_{DSC}}. This could be related to the effect of strain on the size of the crystalline domains. Further discussion is found in Section 3.5.5. Regardless of the melting temperature discrepancy, 12a – 12c, and 13a show thermoplastic elastomer behavior in that they show a rubbery plateau at temperatures between T_g and T_m.

The mechanical properties of 12a – 12c are greatly affected by the oligo(β-alanine) segment length. The plateau modulus, determined from DMA, increases in magnitude with oligo(β-alanine) length. Tensile testing shows a similar trend where the modulus at 10% strain (E_{10%}), and 100% strain (E_{100%}) increase with oligo(β-alanine) segment length (Figure 3.44 and Table 3.5). This is a result of a higher weight % of oligo(β-alanine) providing more reinforcement. 12b and 12c show a pronounced upturn in the stress near 800 % strain. The upturn is not as pronounced in 12a, but there appears to be an inflection point above 800% strain. The exact reason for the upturn has not been determined for these samples, but is not likely due to the strain induced crystallization of butyl rubber because such an upturn is absent in 12a at similar strains. Rather, the upturn must be associated with the increased amount of hard segment. The ultimate strength of the samples follows the same general trend as the modulus.
where longer hard segments give higher strength. The elongation however is similar for each of these polymers.

The hysteresis and tensile set for $12a - 12c$ increase with oligo(β-alanine) segment length. High hysteresis and set are attributable to plastic deformation resulting from the break up of crystalline domains upon straining the sample. It is therefore not surprising that the polymers containing longer oligo(β-alanine) segments require more energy (higher hysteresis) to be broken up and display higher set.
3.5.3 Mixed Grafted Polymers with Piperidine and Oligo(β-alanine) Dimer Grafts

If the presence of piperidine amides in 14b and 14c disrupt the crystalline structure of the oligo(β-alanine) domains, the formation of a physical network could be compromised. This could occur by hydrogen bonding between the N-H of oligo(β-alanine) and the C=O of the piperidine amide. 14c contains crystalline domains as shown by a T_m and T_c in the DSC thermograph in Figure 3.39. The hydrogen bonding structure of these crystalline domains is unperturbed by the presence of the piperidine. This is demonstrated by the absorbance frequency of the amide A, amide I and amide II bands for 12b and 14c being nearly the same (Figure 3.50). 14b shows no observable T_m or T_c by DSC. This may be a result of the crystallizable content being below the detection limit of the instrument as polymer 14b contains only 0.6 wt% crystallizable content. However, the FTIR of 14b does show an amide A band that indicates hydrogen bonding. This band is broader and slightly shifted to a higher wavenumber that the amide A found for 14c and 12b indicating a less ordered, weaker hydrogen bonding structure. The oligo(β-alanine) amide I band is overwhelmed by the C=O band for piperidine, but a small peak at 1554 cm\(^{-1}\) can be observed and gives some indication that the secondary structure of the oligo(β-alanine) in 14b is retained at least to some extent.
Figure 3.50 FT-IR spectrum (from top to bottom) 12b, 14c, 14b, and 14a.
As for the overall utility of using mixed grafted polymers with oligo(β-alanine) and piperidine grafts as a strategy to adjust the grafting density ($M_H$), it is a reasonable approach within some limits. At 4:1 ratio of oligo(β-alanine) dimer to piperidine amide (14c), the system still contains phase separated crystalline domains with the expected secondary structure. At a ratio of 1:7, (14b) the system may be close to the limit of what can be obtained with this approach. Nonetheless, assuming the lower concentration limit of oligo(β-alanine) to be somewhere between a 1:4 and 1:7 ratio, there is still a large range of $M_H$ that could conceivably be synthesized.
3.5.4 Mixed Grafted Polymers with Oligo(β-alanine)s of Different Lengths

The hydrogen bonding structure of polymers 12d and 12e are not disrupted by the presence of oligo(β-alanine)s of different lengths as determined by FT-IR (Figure 3.48). However, the presence of two high temperature (>10 °C) transitions in the temperature sweep DMA experiments and DSC experiments are evidence of the oligo(β-alanine) unimers and trimmers self-sorting into discrete domains in 12e. Because of the low weight percent of oligo(β-alanine) trimer in 12d the trimer melting temperature can only be observed with DMA and not DSC. Nonetheless, 12d also shows self-sorting behavior.

The E’ determined by temperature sweep DMA (Figure 3.43) does not show a plateau between the oligo(β-alanine) unimer and trimer melting temperature transitions. Rather the E’ decreases as temperature increases, and this is more pronounced for 12e than 12d. At similar temperatures (between the two melting temperatures) E’ is higher for 12d than 12e. This is a consequence of the oligo(β-alanine) unimer to trimer ratio being higher in 12d than in 12e.

12d shows similar stress strain behavior to 12a at low strains but at higher strains shows a lower modulus, a higher γb, and a similar σb. The hysteresis and set are nearly the same as 12a. Aside from the higher γb, 12d behaves very similarly to 12a. It is hard to discern any effect brought about by the trimer on the tensile properties. This may be a result of the trimer content being too low for any discernible effects.

12e has an equal molar ratio of unimer and trimer and the total weight percent of oligo(β-alanine) segments in 12d is nearly the same as 12b which is
grafted with only oligo(β-alanine) dimer. This makes for an interesting comparison. The similarity of the stress strain behavior of 12e and 12b lead to the conclusion that the modulus and strength are more related to total oligo(β-alanine) weight percent rather than oligo(β-alanine) segment length. However, 12e shows 14% less set and 4% less hysteresis when compared to 12b. This is very interesting, because in similar systems, increasing the hard segment content also increases hysteresis and tensile set.\textsuperscript{22,33,18} This is demonstrated when comparing polymers 12a, and 12b. In this case, the hard segment is increased from 3.0 wt\% to 4.4 wt\%, and the modulus, strength, tensile set, and percent hysteresis all increase accordingly. However, when comparing polymers 12a and 12e the hard segment again increases from 3.0 wt\% to 4.4 wt\%. The modulus and strength are increased by about the same magnitude as in the case of 12a and 12b, but the tensile set and percent hysteresis do not change. By having oligo(β-alanine) grafts of different lengths, it is possible to change the strength and modulus of the material independent of the hysteresis and set.
3.5.5 Melting Temperatures

The oligo(β-alanine) $T_m$ is dependent on the length of the oligo(β-alanine) segment, the concentration of the oligo(β-alanine) segments in the system, the method of measurement (DSC or DMA), and the size of the terminal groups at the C and N termini of the oligomers. Figure 3.51 shows the melting temperatures determined by either DSC or DMA as a function of oligo(β-alanine) weight percents. For the unimer (green diamonds) and trimers (blue triangles) the fully grafted and oligo(β-alanine) mixed length grafts are shown. For the dimer (red circles) the piperidine mixed grafts are shown. At similar weight percents the $T_m$s increase with oligo(β-alanine) segment length. This is a result of increased hydrogen bonding. At a constant segment length the $T_m$s increase with concentration. $T_m$ dependence on hard segment concentration is commonly reported for segmented TPEs with crystallizable hard segments and is a result of changes in crystalline domain size. Only two data points are shown for the dimer and they have similar weight percents. Further study would be needed to confirm that the trend holds true for dimer.
Figure 3.51 Oligo(β-alanine) domain melting temperatures as a function of weight percent.
The difference between the $T_m$s measured by DMA and DSC may be consequence of strain induced changes in crystal domain size. Gaymans et al. shows that when a segmented TPE with monodisperse crystallizable hard segments is deformed, the crystalline domain size decreases. A decrease in lamellar thickness is known to suppress the melting temperatures of polymer crystals. Therefore it follows that because $T_{mDSC}$ is a measurement of a pristine unstrained specimen with large crystal sizes, the resulting melting temperature is higher. $T_{mDMA}$ is a measure of the melting temperature of a strained specimen with reduced crystal sizes and therefore shows lower melting temperatures. To test this further, $T_{mDMA}$ for 13a was determined at several strain amplitudes and was shown to decrease with higher strains (Figure 3.52). The absence of this melting temperature discrepancy in 12c could be a consequence of the stronger hydrogen bonding in 12c. A strain amplitude of 2% may not decrease the crystal size enough to produce any detectible change.

The $T_m$s of the oligo(β-alanine)s shows a dependence on the bulkiness of the terminal groups at the C and N termini of the oligomer. Polymers 4a – 4d in Chapter 2 have the bulky methoxy aniline and m-toluoyl groups at the C and N termini. Oligomers 11a – 11c in this chapter use the less bulky isobutyl amine at the C terminus and an alkyl chain at the N terminus. Figure 3.53 shows that the $T_m$s of the bulky series require longer oligomer lengths (z) to achieve comparable $T_m$s.
Figure 3.52 DMA determined melting temperature ($T_{mDMA}$) plotted against strain amplitude.

Figure 3.53 Melting temperatures of oligo(β-alanine)s with bulky end groups (red squares) and small end groups (blue diamonds).
3.6 Conclusion

A method has been developed to graft oligo(β-alanine) to butyl rubber through the use of the ene reaction without causing significant chain scission. High strength elastomers were achieved with ultimate strengths in excess of 20 MPa and ultimate strains in excess of 1000%. The oligo(β-alanine) segments phase separate into anti-parallel beta sheet structures similar to those observed for the most prevalent polymorph of Nylon 3. Using a mixed grafting strategy of oligo(β-alanine) pendent groups and piperidine amide pendent groups is a reasonable method to adjust the molecular weight between hard segments \( (M_{hh}) \) that does not disrupt the crystalline structure of oligo(β-alanine). Oligo(β-alanine) segments of different lengths grafted onto the same butyl rubber chain self-sort into discrete domains. By adjusting the segment length ratios, the stiffness and strength of the polymer can be increased independent of the hysteresis and tensile set.
REFERENCES


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APPENDIX A

SHIFT FACTORS FOR POLYMER 4a

Frequency sweep experiments from 0.1 Hz to 100 Hz were performed on 4a from 0 °C to 50 °C at 10 °C intervals to construct a master plot referenced to 0 °C using time temperature super positioning. The Log (aT) is plotted as a function of temperature in Figure A1.

Figure A.1 aT as a function of temperature for polymer 4a
APPENDIX B

COSY SPECTRUM FOR POLYMER 4C

Figure B.1 COSY spectrum for polymer 4c in CDCl₃
Figure B.2 assigned $^1$H NMR spectrum of polymer 4c in CDCl$_3$