THERMOPLASTIC ELASTOMERS WITH OLIGO (β-ALANINE) HARD SEGMENTS

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THERMOPLASTIC ELASTOMERS WITH OLIGO (β-ALANINE) HARD SEGMENTS

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CHAPTER I

INTRODUCTION

1.1 Thermoplastic Elastomer(TPE)

Thermoplastic elastomers display the mechanical properties like vulcanized rubbers at service temperature and can be melt-processed like plastics. The properties come from their multi-segmented structures. The soft segments form the rubbery matrix and the hard segments crosslink the macromolecules by reversible physical or chemical interaction. Multiple types of reversible molecular interactions can be employed: crystallization, phase separation, ionic interactions, or reversible covalent bonds, such as Diels-Alder [4+2] cycloaddition[1]. At the service temperature, the molecular networks are locked by the physical crosslinks. The crosslinks break after solid-to-liquid transitions occur at elevated temperature so that thermoplastic processing methods can be used.

1.2 Styrenic TPE

Styrenic TPE now is one of the most well researched types. With the novel structure of hard-soft-hard domain in middle of 20 century, it gives good mechanical properties due to the well defined microstructure.
1.2.1 Triblock Styrenic TPE

One of the most well studied TPEs is styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) triblock copolymers\textsuperscript{[2][3][4]}. In 1963, Phillips Petroleum Co. first made “Soleprene”, which is a styrene-butadiene-styrene copolymer,\textsuperscript{[5][6]} Lithium initiator was used to obtain a diblock SB copolymer, and the final product was obtained by coupling of the diblock copolymer. In 1965, Shell Chemical Co. developed a three-step anionic method to produce SBS and also made a styrene-isoprene-styrene copolymer\textsuperscript{[7][8]}. These successes marked the beginning of thermoplastic elastomer research and commercialization.

In the late 1960s, Phillips Petroleum Co. developed a star shape styrenic copolymer. Comparing to linear copolymer, resistance to cold flow, processability, and high temperature performance were improved\textsuperscript{[9]}. For SBS and SIS, both of them suffered aging due to the presence of unsaturated carbon-carbon double bonds. In 1974, Shell Chemical Co. developed a hydrogenation technology, which solved the aging problem and increased the service temperature\textsuperscript{[10][11]}.

1.2.2 Phase Separation in Styrenic Triblock Copolymers

The styrenic tri-block copolymers contain two styrene end blocks and a elastomeric middle block. Below the order-disorder transition temperature, the styrene blocks microphase separates from the soft rubbery matrix. The styrene domains have a higher glass transition temperature ($T_g$) than the rubbery butadiene domains and are hard domains. The hard domains physically crosslink material and work as a filler to reinforce the material. The
preferred morphology for TPEs is shown in Figure 1, where the spherical polystyrene domains are surrounded by the soft rubbery component.

![Figure 1. Schematics of a SBS structure](image)

At elevated temperatures above its glass transition temperature, the hard domain softens, allowing the flow of the material. At such temperatures, the material is processed. The styrenic domains harden again upon cooling below the glass transition temperature. The process is reversible. This property enables the reprocessibility of SBS thermoplastic elastomer.[13]

1.3 Thermoplastic Polyurethane (TPU)

In 1958, the first polyurethane has been made by Schollenberger. It’s also the first thermoplastic made by human being. During the following years, companies around the world started producing small scale polyurethane, such as “Texin” made by Mobay Chemical Co., “Estane” made by B. F. Goodrich Chemical Co., and “Pelletane” Upjohn Co., etc[10][14].

Polyurethane was polymerized by coupling diisocyanate acid and dio[15][16][17], and two
types of segments were joined by covalent -NH-COO- bonds. The polyurethane elastomer materials are composed of low glass transition temperature segment (soft segment) and rigid urethane segment (hard segment) alternatively \[15\]. Therefore, polyurethane materials are considered as a multiblock copolymer \[18\]. Due to the polarity differences of hard and soft segment, microphase separation occurs on a molecular level \[19][20][21][22\]. As Shown in Figure 2, the hard semi-crystalline domains physically crosslink and reinforce the polymer, while the soft domain still produce rubber elasticity at the service temperature.

![Figure 2. Segment structure of polyurethanes\[23\]](image)

1.4 Supramolecular Networks

Supramolecular networks are formed by customized, highly directed supramolecular bonds such as hydrogen bonds, π-π interactions, or metal complexes, either assemble non-covalently associating monomers to networks chains, or connect isolated covalently associating polymer chains \[24\]. Like most of thermoplastic elastomers crosslink interaction, the supramolecular interaction is a kind of thermoreversible physically interaction. With elevating temperature, de-crosslink occurs easily, while at service temperature it forms strong material.
Three major advantages can be obtained with the utility of physical crosslinked polymer network: first, the reversible of crosslinking allows the material reprocessibility; second, self-healing properties were obtained in supramolecular polymer materials; third, shape-memory materials can be obtained if combined with covalent crosslinks.  

1.4.1 Hydrogen Bonding

Hydrogen bonds are interaction between a proton connect to an electron-withdraw atom (donor) and a lone electron pair on an electron-rich atom (acceptor). With elevating temperature, single hydrogen bond weakens significantly. With inspiring of nature, the double or triple hydrogen bonding arrays can be employed to improve the strength of interactions.

1.4.2 Natural Silk Material

Natural silk is a strong and tough biological material with multiple segments structure. Spider silk and silkworm silk are most researched by human. As one of the strongest and toughest material known, silk has been used in diverse technological application such as medical sutures, parachutes, bullet proof vest, and more recently, tissue regeneration.

–GlyAlaGlyAlaGlySer- has been determined to be the primary peptide sequence for Bombyx mori silk fibroin; and -Ala_n- for Nephila clavipes silk. These β-sheet forming sequences alternate with amorphous segments composed of amino acids, some of which have bulky side groups. Recent researches show that the antiparallel β-sheet microstructures, which play a key in defining silk mechanical properties by providing stiff orderly crosslinking domains embedded in a semi-amorphous matrix that consists predominantly of less orderly β-structures. β-Sheet structures have a few nanometers dimensions and constitute
approximately 10-15% of silk volume. When stretching happens to silk, the β-sheet microstructure reinforces the silk by transferring the load between chains under lateral loading.

1.4.3 β-alanine Crosslinked Thermoplastic Elastomer

β-sheet is a secondary structure of peptide, which is formed via hydrogen bonds between peptide chains. The β-sheet structure is shown in Figure 3.

Due to electronegativity, the proton which is directly connecting to nitrogen atom becomes a hydrogen bond donor, while the electron pair of carbonyl group oxygen makes itself a good acceptor. Peptide chains aggregate together by hydrogen bond interaction and align in three dimensions to form β-sheet\cite{26}\cite{27}.

Nylon 3 takes the advantages of hydrogen bonds and forms anti-parallel β-sheets, which stack on top of each other to form a crystalline material. Oligo(β-alanine)s are oligomers of Nylon 3(2-8 residues). They can also form anti-parallel β-sheets. Oligo(β-alanine)s have better solubility in conventional solvents than nylon 3 and are easier to process since their decomposition temperature is higher than their melting temperatures\cite{28}.

![Figure 3. The structure of a section of β-sheet formed by β-alanine oligomer](image-url)
1.5 Design of β-sheet Crosslinked TPEs

In this work, two types of thermoplastic elastomer were made: low molecular weight oligo(β-alanine) end-functionalized polybutadiene, and high molecular weight oligo(β-alanine)-grafted polyisobutylene. We expect that the oligo(β-alanine)s in the material undergo microphase separation to form β-sheets. The hard peptide domains crosslink the material physically and reinforce it. With the use of supramolecular crosslinker, materials with good mechanical are expected.

![Figure 4. Expected β-sheet crosslinked TPE structure](image-url)
CHAPTER II

OLIGO(β-ALANINE) END-FUNCTIONALIZED POLYBUTADIENE

2.1 Results and Discussion

A polybutadiene end functionalized by oligo(β-alanine) trimer was made. Combining all the information, microstructure separation was observed, but it doesn't gave the material good mechanical properties, that due to the low molecular weight of PBD.

2.1.1 Coupling of Telechelic PBD with Oligo(β-alanine)

Figure 5 shows the NMR spectrum of the telechelic carboxylic acid-terminated polybutadiene, which was used as the starting material for oligo(β-alanine) end functionalization. The number average molecular weight is about 5500g/mol. The two peaks around 5.42ppm and 5.39ppm are olefin group from trans and cis 1,4-configuration of backbone respectively. And the singlet at 2.09ppm and 2.05ppm are the peaks of methylene group of 1,4- configuration. As for 1,2- configuration, the multiplet at 4.98ppm and singlet at 1.46ppm are olefin and methylene group respectively. The multiplet at 2.58ppm comes from the end group of polymer. As expected, this peak should disappear completely after reaction, but not, as shown in Figure 6. The peak shift a little to 2.50ppm with a shoulder. And experiment condition was adjusted when repeat this experiment, such rising temperature, adding more peptide/EDC coupler, but didn't help.
From the spectrum, not only multiplet can be seen, also several peaks overlap there. Peaks other than end group overlap there is possible. This means there are peak inreactive with
peptide segment. COSY spectrum was done to investigate this peak, and that idea was demonstrated.

The peak at 2.58ppm correlated with two other peaks. In Figure 7, PBD COSY spectrum is showing, the peak at about 2.60ppm comes from the starting material. Also a light dot shows that peak correlate with another peak at about 2.20ppm, in methylene area of polybutadiene. After activated by the succinimide, the peak shifts to about 2.80ppm. At 2.58ppm, there still is a peak didn’t change, and still correlate with the peak in methylene area. That means this group isn’t reactivity end group, and will not be activate by succinimide, neither the oligo(β-alanine). So this doesn’t come from the reactivity end group.

NMR spectrum of trimer functionalized PBD has shown as Figure 6, the polybutadiene didn’t change same as in non-functionalized one in Figure 5. Compare with oligo(β-alanine)trimer NMR spectrum Figure 8, the doublet caused by end iso-butyl group at 0.92ppm still appears, also the multiplet at 1.78ppm caused by ternary hydrogen on iso-butyl group. Peaks of methylene groups on oligo(β-alanine) backbone changed a lot. In the polymer they overlapped at 2.35ppm and 3.53ppm, which can be distinguished in trimer. And
amine peaks are ranging from 6ppm to 7ppm in functionalized polymer. Also the Figure 6 shows a peak indicating the presence of methanol, which comes from the work up step of polymer products. A completely reacted trimer functionalized polymer was obtained.

Figure 8. $^1$H NMR spectrum of Ala$_3$
2.1.2 Structure Characterization

The structure information was obtained by NMR and IR method; thermal properties were obtained by TGA and DSC method; and mechanical properties were obtained by tensile test.

2.1.2.1 TGA Result

TGA test was conducted in order to get the decomposition temperature of the material, so that the process condition can be controlled. The test was under N₂ atmosphere. The TGA curve is shown in Figure 9 below. TGA shows the material start decomposition at 210℃, and this process till 480℃. In this process, two decomposition temperatures can be observed at about 300 ℃ and 400 ℃ respectively. They must be β-alanine and polybutadiene decomposition respectively. Extrapolate from TGA curve, decomposition temperature of the material can be obtained, is 420℃. When start heating, a small increment of mass can be seen. That most probably caused by the gravity moving during the melting process. The increasing started at about 170 ℃, which consist with the melting temperature obtained by DSC.

![TGA curve of Ala₃-PBD-Ala₃](image-url)
2.1.2.2 FTIR Result

The FTIR was conducted at room temperature. The sample was prepared on KBr salt plate by CHCl₃ casting. The spectrum is shown in Figure 10 below. β-sheet is a secondary structure of peptide formed by hydrogen bond. In this kind of secondary structure, the stretching frequency of amide is sensitive to IR vibration. Strong infrared band around 1630 cm⁻¹ will be given to indicate the antiparallel β-sheet conformation. In Figure 10, the peak at 1630 cm⁻¹ indicates the antiparallel β-sheet in copolymer. The peaks between 1630 cm⁻¹ and 1700 cm⁻¹ indicate conformation choices other than β-sheet. But in Figure 10, there aren’t any sign of these peaks. In the copolymer, the short peptides are mostly form β-sheet rather than other conformation[29]. Also, the strong peak appearing at 3290 cm⁻¹ in amide A region indicates the hydrogen bonds predominate the conformation. But it’s more like an interchain type β-sheet, which was desired[30],[31].

Figure 10. FTIR spectrum of Ala₃-PBD-Ala₃
2.1.2.3 DSC Result

In order to get the desired mechanical properties, phase separation should be clearly defined. Thus, the hard peptide and soft polybutadiene domains exhibit their own properties. Peptide domains form physical crosslink, and also may serve as a filler to reinforce the material\textsuperscript{[28][32]}. DSC was used to investigate this property, and heat compress film was used. And the DSC trace is shown in Figure 11 below.

Two heating cycle was conducted under nitrogen atmosphere, and the heat trace was recorded from 50°C of first cycle. The DSC trace shows first-order transition occurred at 185°C in Ala\textsubscript{3}-PBD-Ala\textsubscript{3}, which correspond to the melting temperature of hard segment, which is Ala\textsubscript{3} peptide crystal. When crystallizing, peaks not only shown at 180°C, also at 170°C, which indicates another crystallization temperature of alanine crystal. These double peaks may due to different crystal structure or peptide conformation. And the transition at -83°C indicates the glass transition of polybutadiene. The melting temperature of oligo(β-alanine) is much higher than reported 120°C\textsuperscript{[33]}. The glass transition temperature didn’t change a lot,
which consisted with the melting point of polybutadiene used in the copolymer. When second cycle was applied, the melting peak and glass transition peak don’t change.

2.1.2.4 Tensile Test Result

The mechanical properties of peptide functionalized polymer were investigated by stress-strain curve, at room temperature. Samples were prepared by heat compress. Sample were heated to 185°C under 3,000 lbs. When the temperature reached 185°C, increased the pressure to 15,000 lbs for 30 seconds then released, repeated 2 times. After turned off heat and the film was allowed cooling down. Whole processes were done under nitrogen atmosphere. Film cut into dumb bell specimen by ASTM D638 type V dies. The elongation at break, modulus, and tensile strength was obtained. Representative stress-strain curve is shown in Figure 12.

![Figure 12. Stress-strain curve](image-url)
Table 1. Mechanical properties of functionalized polymer

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<th>Modulus</th>
<th>Tensile strength</th>
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<tr>
<td>Ala₃-PBD-Ala₃</td>
<td>12.1%±1.4%</td>
<td>20.4MPa±0.3MPa</td>
<td>1.3MPa±0.1MPa.</td>
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Due to the phase separation, the peptide domain serves as filler to reinforce the material. The tensile strength is similar to Ala₂-PBD-Ala₂, the dimer functionalized polymer made in our lab before. And the modulus of trimer polymer is about 4 times higher than dimer polymer. But the elongation break is much lower. The lower elongation may cause by low molecular weight of polybutadiene. Also the unsaturated may be the reason of poor mechanical. The causes of mechanical are still further research.
2.2 Experiment

A polybutadiene end functionalized by oligo(β-alanine) trimer is made. All synthesis steps were done in solution phase, including peptide synthesis, polymer activation and functionalization.

2.2.1 Synthesis of Oligo(β-alanine)

The trimer alanine was prepared by stepwise condensation in DCM or DMF, shown in Scheme 1, starting with protected β-alanine Boc-Ala-OH and NH$_2$-Ala-Bz, to give compound 8. The liberation of amino group from Boc-peptide in stepwise elongation was carried out by 3M HCl/EA, followed by vacuum evaporating the solution. Thus, from the protected peptide 3, 7 got the free amino group of 4, 8 respectively. Removal of the benzyl group from 5 was performed by hydrogenolysis using Pd/C as a catalyst in CHCl$_3$, and the products 6 was ready for next step condensation. Iso-butyl group was used as a cap of peptide, the condition same as peptide coupling. With repeating these deprotecting then coupling procedures, peptides in any length of repeat units can be obtained. The trimer peptide was tested by $^1$H-NMR in DMSO. $^1$H NMR (300 MHz, DMSO, d, ppm) 8.00 (overlapped s, -NH$_2$ and –NH, 5H), 3.23 (overlapped p,4H), 2.94 (q, N-CH$_2$-CH(CH$_3$)$_2$,2H), 2.85 (t,2H), 2.46 (t,2H), 2.23 (overlapped q,4H), 1.65 (m, -CH(CH$_3$)$_2$,1H), 0.82 (d, -CH(CH$_3$)$_2$,6H).
Scheme 1. Synthesis step of oligo (β-alanine)
2.2.2 Coupling of the Oligo(β-alanine) with the Telechelic PBD

As shown in Scheme 2, 1eq. polybutadiene and 4eq. succinimide was added to Schlenk flask and pumped for an hour. Then 10eq. anhydrous TEA was added under nitrogen flow. Chloroform was used as solvent, make the polymer concentration at 0.05mol/L. The reaction solution was stirred overnight. Pumped out all the solvent and washed the polymer with hex till the all TFA gone. Then under N\textsubscript{2} atmosphere, added succinimide activated polybutadiene 1eq. and 2.5 eq. trimer. Then added 10 eq. TEA, dissolve in DCM:DMSO=50:1 volume ratio. Reaction solution was stirred under N\textsubscript{2} flow at room temperature overnight.

![Scheme 2](image)

The polymer was precipitated by methanol and pumped overnight. Then NMR test in CDCl\textsubscript{3}, \textsuperscript{1}H NMR 500 MHz, CDCl\textsubscript{3}, d, ppm, the multiplet at 5.41ppm, 5.38ppm indicate trans- and cis- olefin protons respectively; The multiplet at 4.97ppm indicates 1,4 olefin protons; The singlet at 4.97ppm indicates 1,4 olefin protons 2.08ppm, 2.04ppm indicate cis- and trans- methylene protons respectively; the singlet at 1.30ppm indicates the olefin protons of 1,4 production. The multiplet overlapped at 3.53ppm and 2.36ppm indicates the methylene protons of β-alanine. The multiplet at 3.08ppm indicates the methylene protons of iso-butyl group. The multiplet at 1.78ppm indicates the methyne protons of iso-butyl group. The doublet at 0.92ppm indicates the methyl protons of iso-butyl group.
CHAPTER III

OLIGO(β-ALANINE) GRAFTED BUTYL RUBBER

3.1 Results and Discussion

Butyl rubbers grafted with oligo(β-alanine) dimer and trimer were made. Combine all the information, microstructure separation was observed, it gave the material good mechanical properties.

3.1.1 Synthesis & Characterization of Oligo(β-alanine) Grafted Butyl Rubber

Commercial butyl rubber is isobutylene and isoprene copolymer, and the isoprene content is less than 3%[33]. The butyl rubber used in the present work was donated by Goodyear. Its $^1$H-NMR spectrum is shown in Figure 13. According to the previous reported[33], peaks a and b at 1.42ppm and 1.11ppm are due to methylene and methyl repeat units of the isobutylene respectively. The peak at 5.08 ppm arises from the isoprene units. Integration ratio of this peak to the isobutylene peak shows that the isoprene content is 1.4% by mole. In other words, the number-average molecular weight between two isoprene units is about 4,000g/mol. GPC shows the molecular weight is $4.86 \times 10^5$, PDI=1.22. The peak at 1.95ppm arises from methylene group on the isoprene units. The methyl group on isoprene appears at 1.65ppm.
The above butyl rubber 1, was used in this work as the starting material for grafting oligo(β-alanine) as shown in Scheme 3. Following the method reported by Gillies et al\textsuperscript{[35]}, 1 was epoxidized by 3-chloroperoxybenzoic acid (MCPBA) in toluene to give 2. The result of epoxidation varied somewhat from batch to batch. The resultant epoxy content ranged from 1.4\% to 1.1\% by mole estimated from NMR integration\textsuperscript{[35]}. This corresponds to quantitative to 78\% conversion of the double bonds to the epoxy structure.
According to the literature work, acid was used to convert the epoxide to give an alcohol structure. In my hands, this procedure didn’t go as reported. Elimination occurred instead to give structure 5 shown in Scheme 4.

![Scheme 4](image)

Scheme 4. Elimination structure

An alternative method then was used. Polymer 2 was refluxed with 4-nitrophenyl chloroformate in the presence of pyridine to directly produce polymer 3. From 1 to 3, the molecular weight didn't change appreciably, which can be seen in experimental section. The activated polymer 3 was reacted with oligo(β-alanine) to obtain 4a and 4b. Due to β-sheet aggregation, the oligo(β-alanine) solubility is not good in chloroform. In order to break the hydrogen bonded β-sheet, trifluoroethanol(TFE) was first used. The oligo(β-alanine)s dissolved better, but TFE caused a new problem. The p-nitrophenyl carbonate is reactive toward TFE as well to give the TFE carbonateas shown in Scheme 5.

![Scheme 5](image)

Scheme 5. Reaction of 3 with TFE

DMSO was then used as an alternative choice to break hydrogen bond aggregation in peptide while not reacting with 3. Refluxing the oligo(β-alanine) and 3 in chloroform in the presence of DMAP and DMSO give 4a and 4b. The progress of the reaction can be
monitored by $^1$H NMR. As shown in Figure 14, the nitrophenolate peaks at 7.39ppm and 8.28ppm disappeared when the reaction was complete.

![Diagram](image)

Figure 14. $^1$H NMR spectra of 3 and 4a

$^1$H NMR spectra of 4a and 4b and peak assignments are shown in Figure 15. The oligo(β-alanine) methylene peaks appear at 3.53ppm and 2.40ppm. The peak at 3.09ppm is due to the methylene on the isobutylamine end cap. The integration of the end cap peak at 3.09ppm and butyl rubber units at 1.42ppm were used to estimate the peptide content. By this method, the peptide contents of dimer and trimer grafted polymer were 1.1mol% and 1.4mol%, respectively. Due to the grafted polymer poor solubility in THF, the molecular weight of 4a and 4b cannot be get by the GPC.
Figure 15. $^1$H NMR spectra of 4a and 4b in CDCl$_3$
3.1.2 Thermal Characterization

Thermal stability of 4a and 4b was tested by TGA under a nitrogen atmosphere. The TGA curves are shown in Figures 16 and 17. Their thermal decomposition processes were summarized in Table 2. The peptide grafted polymers exhibit a good thermal stability upon approximately 230°C, where polymers started decomposing. The thermal stability of these two polymers is similar. From both polymers, two close decomposition temperatures can be observed, which correspond to oligo(β-alanine) and butyl rubber, respectively. 5% weight loss temperatures (T₅) are important evidences of thermal stability. These results are indicating all these two oligo(β-alanine) grafted polymers have a good thermal stability at elevated temperatures. The decomposition process was going until over 400°C.

![TGA curve of 4a](image)

Figure 16. TGA curve of 4a
Figure 17. TGA curve of 4b

Table 2. Thermal decomposition of 4a and 4b

<table>
<thead>
<tr>
<th>°C</th>
<th>T5</th>
<th>T20</th>
<th>T50</th>
<th>T70</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB-g-Ala2</td>
<td>290</td>
<td>345</td>
<td>373</td>
<td>385</td>
</tr>
<tr>
<td>PIB-g-Ala3</td>
<td>286</td>
<td>344</td>
<td>375</td>
<td>386</td>
</tr>
</tbody>
</table>

DSC was performed under a nitrogen atmosphere to investigate the thermal properties. Two heating-cooling cycles were applied. And both curves are displayed in Figure 18 and 19.
Figure 18. DSC curve of 4a

In both polymers, the glass transition peak was found around -70°C, which is attribute to polyisobutylene segment. The $T_g$ is a few degrees higher than butyl rubber data. For dimer
grafted polymer, there is a broad peak shown start around 187°C, which correspond to the oligo(β-alanine) dimer melting. For the trimer grafted polymer, the broad melting peak started at about 206°C. These two melting peaks are both very broad and difficult to recognize.

To get a clear, well define melting point, DMA was conducted. The DMA curves of 4a are shown in Figure 20.

The storage modulus has a broad dropping start from about 100°C until almost 180°C. The melting point can be obtained here is 129°C. The reason this peak broad may be caused by the merging of oligo(β-alanine) dimer melting peak and a certain thermal transition peak of butyl rubber around 100°C. This can be confirmed in trimer grafted polymer DMA.

![Figure 20. DMA curve of 4a](image-url)
The DMA curve of 4b is shown in Figure 21. The storage modulus has two well distinguished steps dropping at 100°C and 140°C. And the second step is melting peak, where melting temperature can be obtained is 139°C. And the first step was around 100°C, which can explain the broad melting peak in 4a.

Figure 21. DMA curve of 4b
3.1.3 FTIR Result

FTIR test was carried out at room temperature. Sample was prepared by CHCl₃ casting onto KBr salt plate. FTIR spectrum of 4a is shown in Figure 22 with assignment of major peptide peaks in Table 3. The band at 3300 cm⁻¹ is attributed to amide N-H (amide A) vibration, while amide I and amide II band can be observed around 1650 cm⁻¹ and 1545 cm⁻¹.

![FTIR Spectrum of 4a](image)

**Figure 22. FTIR spectrum of 4a**

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>Amide N-H (amide A)</td>
</tr>
<tr>
<td>1715</td>
<td>Urethane C=O</td>
</tr>
<tr>
<td>1650</td>
<td>Amide C=O (amide-I)</td>
</tr>
<tr>
<td>1545</td>
<td>Amide N-H (amide-II)</td>
</tr>
</tbody>
</table>
FTIR spectrum of 4b is shown in Figure 23 with assignment of major peptide peaks in Table 4. The band at 3300 cm\(^{-1}\) is attributed to amide N-H (amide A) vibration, while amide I and amide II band can be observed around 1645 cm\(^{-1}\) and 1550 cm\(^{-1}\).

![Figure 23. FTIR spectrum of 4b](image)

**Table 4. Assignment of 4b FTIR**

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>Amide N-H (amide A)</td>
</tr>
<tr>
<td>1700</td>
<td>Urethane C=O</td>
</tr>
<tr>
<td>1645</td>
<td>Amide C=O (amide-I)</td>
</tr>
<tr>
<td>1550</td>
<td>Amide N-H (amide-II)</td>
</tr>
</tbody>
</table>

These results indicate oligo(\(\beta\)-alanine) is hydrogen bonded. There are no peaks other than amide-I peak showing between 1630 cm\(^{-1}\) and 1700 cm\(^{-1}\) indicates \(\beta\)-sheet is the only conformation of oligo(\(\beta\)-alanine)\(^{[29]}\). And the strong peak appearing at 3300 cm\(^{-1}\) in amide A region indicates the hydrogen bonds predominate the conformation. It’s an desired interchain type \(\beta\)-sheet\(^{[30]}\)\(^{[31]}\).
3.1.4 Tensile Test Result

The tensile curve of 4a is shown in Figure 24. The tensile curve of 4b is shown in Figure 25. Two samples of each polymer were tested.

Figure 24. Stress strain curve of 4a

Figure 25. Stress strain curve of 4b
The tensile properties are summarized in Table 5. Both polymers show a typical elastomer behavior, high elongation before failure and no obvious yield points were observed. Elongation at break and tensile strength for dimer grafted polymers are 1485% and 8MPa respectively, 1160% and 12MPa for trimer grafted polymer. As expectation, the trimer polymer is stronger than dimer polymer, which should be attributed to the length of peptide. The longer peptide is the stronger interaction they form. And dimer grafted polymer is softer and more ductile.

Table 5. Summary of mechanical properties of 4a and 4b.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Stress at certain strain (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100%</td>
</tr>
<tr>
<td>PIB-g-Ala$_2$</td>
<td>8.6</td>
<td>1485</td>
<td>0.49</td>
</tr>
<tr>
<td>PIB-g-Ala$_3$</td>
<td>12.2</td>
<td>1160</td>
<td>1.38</td>
</tr>
</tbody>
</table>

a. Data are average of two runs using a new sample for each run. The number in the parenthesis is the difference between the two runs.
3.2 Experimental Section

The materials and reagent used are listing here. And test equipment and parameter settings are showing here as well.

3.2.1 Materials

β-Alanine, di-tert-butyldicarbonate, 4-dimethylaminopyridine, 1-ethyl-3-(3-di-methyl-aminopropyl)-carbodiimide hydrochloride were purchased from Oakwood; Chlorotrimethyl silane, benzyl alcohol, 3-chloroperbenzoicacid, 4-nitrophenyl chloroformate and anhydrous solvents were purchased from Sigma-Aldrich; N-methyl morpholine were purchased from Fluka and Sigma-Aldrich; Pd/C catalyst was purchased from Alfa Aesar and Sigma-Aldrich. Butyl rubber was donated by Goodyear. DMSO was distilled under low pressure.

3.2.2 Characterization Method

Solution NMR spectra were recorded on Varian Mercury 300 and Varian NMRS 500-01 instrument. FTIR spectra were recorded on Digilab Excalibur FTS 3000 series FTIR Spectrometer, FTIR samples were prepared by solution casting on KBr salt plate. DSC was performed on DSC Q2000 V23.13 Build 104, and temperatures were ramped at 10°C/min. TGA was performed on TGA Q500 V20.7 Build 32, temperatures were elevated at 10°C/min. Tensile test samples were prepared on a heat compress machine. Films were cut into dumb bell specimen by ASTM D638 type V mini die. The specimen was stretch by TA Instruments RSA3 Dynamic Mechanical Analyzer, at rate of 100mm/min. DMA was
performed on TA Instruments RSA3 Dynamic Mechanical Analyzer, at 1Hz, 2% strain, 5°C/min heating rate.

Testing films were cast from chloroform. For each polymer, 0.5g was dissolved into about 10ml chloroform to get a slight viscous solution. Then solution was poured into 50*50mm Teflon mold and loosely covered by aluminum foil. The solvent was allowed to evaporate at room temperature overnight, and subsequently pump out left solvent under vacuum at 50°C for 5 h. A transparent, flexible film was obtained with a thickness of about 0.2mm. Films were cut into dumb bell specimen by ASTM D638 type V dies.

3.2.3 Synthesis

Butyl rubbers end functionalized by oligo(β-alanine) dimer and trimer were made. All synthesis steps were done in solution phase, including peptide synthesis, polymer activation and functionalization. The peptide synthesis procedure is same as the method in chapter II.

3.2.3.1 Synthesis of Epoxidized Butyl Rubber 2

5.23 g (2.58 mmol carbon-carbon double bond) butyl rubber was dissolved in 200 ml toluene. 2.97 g 3-chloroperbenzoic acid (purity 74.5%, 12.82 mmol) was dissolved in 100 ml toluene and dried over by sodium sulfate. Then 3-chloroperbenzoic acid solution was poured into polymer solution and stirred overnight at room temperature. The reaction solution was then precipitated into 500 ml acetone. $^1$H NMR (500 MHz, CDCl$_3$, d, ppm): 2.71 (br s, 1H), 1.42 (s, CH$_2$ PIB, 116H), 1.11 (s, CH$_3$ PIB, 348H). Average Mn=4.26*10$^5$, with PDI=Mw/Mn=1.21.
3.2.3.2 Synthesis of 4-nitropheny Carbonate Activated Butyl Rubber 3

5.16g epoxidized butyl rubber (1.50 mmol) was dissolved in 200 ml chloroform. The reaction mixture was stirred at room temperature for 1 hour. Then 2.06 ml (25.59 mmol) pyridine was added dropwise followed by 5.18 g (25.70 mmol) 4-nitrophenyl chloroformate. The reaction solution was refluxed for 3 days. Then polymer was precipitated into about 500 ml acetone. $^1$H NMR (500 MHz, CDCl$_3$, d, ppm): 8.27 (d, J= 8.5 Hz, 2H), 7.40 (d, J=8.5 Hz, 2H), 5.28 (s, 1H), 5.12 (br s, 1H), 5.02 (s, 1H), 1.42 (s, CH$_2$ PIB, 190H), 1.11 (s, CH$_3$ PIB, 570H). Average Mn=4.25*10$^5$, with PDI=Mw/Mn=1.23.

3.2.3.3 Synthesis of Oligo-β-alanine Grafted Butyl Rubber 4a and 4b

Synthesis of oligo-β-alanine used in this step is the same as last chapter.

For dimer grafted polymer: Activated butyl rubber 2.08 g (0.30mmol activated spots) was dissolved in 80 ml chloroform. Then alanine dimer 0.23g (0.92mmol), 4-dimethylaminopyridine 0.11 g (0.92mmol) and 0.5ml DMSO were added into reaction solution. The reaction mixture was refluxed for 3 days. Then product was precipitated into100 ml methanol twice and subsequently pumped by vacuum oven for 6 hours. $^1$H NMR (500 MHz, CDCl$_3$, d, ppm): 3.53 (s, 4H), 3.06 (s, 2H), 2.40 (s, 4H), 1.42 (s, CH$_2$ PIB, 89H), 1.11 (s, CH$_3$ PIB, 267H).

For trimer grafted polymer: Activated butyl rubber 2.22 g (0.32mmol activated spots) was dissolved in 80 ml chloroform. Then alanine trimer 0.36g (1.11mmol), 4-dimethylaminopyridine 0.13 g (1.07mmol) and 0.5ml DMSO were added into reaction solution. The reaction mixture was refluxed for 3 days. Then product was precipitated
into 100 ml methanol twice and subsequently pumped by vacuum oven for 6 hours. \( ^1 \)H NMR (500 MHz, CDCl₃, d, ppm): 3.53 (s, 6H), 3.06 (s, 2H), 2.40 (s, 6H), 1.42 (s, CH₂ PIB, 73H), 1.11 (s, CH₃ PIB, 219H).
CHAPTER IV

CONCLUSION

Inspired by the β-sheet nanostructure of nature silk, the oligo(β-alanine)-functionalized polybutadiene and butyl rubber were made. FTIR indicates intermolecular hydrogen bonding characteristic of β-sheets formation is present in the copolymer. For the end-functionalized polybutadiene, DSC trace shows well-defined melt transitions due to the phase-separated β-sheet crystalline domains. The melt transition was not obvious in grafted copolymer. Mechanical test result shows that the end functionalized polybutadiene was weak. For the grafted polymer, the good mechanical properties were obtained.
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