Chapter 3

Enzymatic Synthesis of Fully Biobased Saturated and Unsaturated Aliphatic Polyesters by Using Different Monomer Substrates and Polymerization Methods

Abstract: Fully biobased saturated and unsaturated aliphatic polyesters and oligoesters are successfully prepared by Candida antarctica lipase b (CALB)-catalyzed polycondensation of succinate, itaconate, and 1,4-butanediol. The effects of monomer substrates and polymerization methods on the enzymatic polycondensation are investigated. The CALB-catalyzed polycondensation with dicarboxylic acids yield oligomers. By replacing the unactivated dicarboxylic acids with alkyl diesters, polyesters with various chemical compositions are successfully obtained. The molar compositions and molecular weights of the obtained poly(butylene succinate-co-itaconate)s (PBSIs) are significantly affected by the applied polymerization method. Compared to the two-stage enzymatic polymerization in bulk and in diphenyl ether, the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene is the best method to synthesize high molecular weight PBSIs with tunable molar compositions. The $^{13}$C-NMR study reveals that CALB is capable of producing more 1-B-I-3 microstructures in the mixture of cyclohexane and toluene by azeotropic distillation. Moreover, the crystalline properties of the obtained polyesters are characterized; and the thermal and mechanical properties of the cross-linked PBSI are studied.

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3.1 Introduction

Unsaturated polyesters are one of the most important classes of cross-linkable thermoset resins.\(^1\) Their global demand amounted to 4.306 million tons in volume with the value of $6.54 billion in 2012.\(^2\) They have been widely used for the manufacture of tanks, pipes, construction, automotive, appliances, and so on.\(^2-4\) The most common unsaturated polyesters are prepared by polyesterification of saturated and unsaturated dicarboxylic acid derivatives, diols, and polyols in the presence of metallic catalysts.\(^1\) Most of these building blocks are derived from depleting petroleum resources. Alternatively, many recently emerging biobased monomers are promising candidates for unsaturated polyester synthesis.\(^5-10\) They are suitable for the preparation of various commodity and novel polyesters since abundant functional green chemicals, like carboxylic acid derivatives, diols, and polyols, are readily produced from yearly-based biomass feedstocks. By utilizing such renewable compounds, the generation of waste and emission will be greatly reduced in the polymer industry. This provides an opportunity to achieve future sustainability.\(^9-13\)

Lipases are versatile enzymes in biocatalytic polyester synthesis.\(^14-20\) Among them, \textit{Candida antarctica} lipase b (CALB) immobilized on acrylic resin (commercially available as Novozym\textsuperscript{®} 435) is the most favorable biocatalyst since it works well with diverse monomer substrates at mild temperatures and even at elevated temperatures.\(^21-23\) So far most research in this field still focused on the enzymatic polymerization of conventional petroleum-based monomers.\(^24, 25\) The use of biobased monomers in biocatalytic approaches towards polyester materials is an appealing topic both in the academic and industrial fields. It has gained increasing popularity in recent years.\(^26-35\)

In our group, we have successfully prepared many polymers via enzymatic polymerizations.\(^36-43\) Recently we reported a total green approach for the synthesis of unsaturated poly(butylene succinate-\textit{co}-itaconate)s (PBSIs) by CALB-catalyzed copolymerization of biobased diethyl succinate, dimethyl itaconate and 1,4-butanediol.\(^38\) We found that the molar percentage of the unsaturated monomeric segments, itaconate units, can be tuned from 0 to 24 mol % by adjusting the molar feed ratio of itaconate from 0 to 25 %. However, further increase of the itaconate feed ratio up to 30 mol % or more led to a significant reduction in the incorporation ratio of itaconate and lower molecular weights. We attributed this to the relatively lower enzymatic polymerizability of itaconate which is caused by its short chain length and the stereo-hindrance effect of the carbon-carbon double bond suspended to the carbonyl group.
In order to synthesize PBSIs with controllable molar compositions and high molecular weights, two additional polymerization methods, the two-stage enzymatic melt polymerization and the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene, are introduced here, using diethyl succinate, dimethyl itaconate and 1,4-butanediol as the starting materials. Among the tested polymerization methods, melt polymerization is the most convenient and straightforward approach, which has been applied dominantly in the industrial field for polyester synthesis. Azeotropic polymerization is another popular method which is frequently applied in step-growth polycondensations. By azeotropic distillation, low molar mass byproducts can be continuously removed and this facilitates the chain growth of polymers. Azeotropic polymerization has been well studied for the production of several biobased polyesters like poly-L-lactide (PLLA), isosorbide polyesters, and unsaturated isoohexide polyesters. Besides, the two-stage enzymatic polymerizations in diphenyl ether always resulted in high molecular weight aliphatic polyesters as reported in literature.

In addition, compared with alkyl diesters, unactivated dicarboxylic acids like succinic acid and itaconic acid, are cheaper and good polyester building blocks. In this work, the CALB-catalyzed dehydration polycondensation of succinic acid, itaconic acid and 1,4-butanediol via the aforementioned polymerization methods is also studied. Moreover, the microstructures of the synthesized PBSIs are investigated by \(^{13}\text{C-NMR}\) technique, to reveal the mechanism of enzymatic polycondensation in different media; and the crystalline properties of the obtained polyesters are characterized by WAXD and DSC. Furthermore, the obtained unsaturated polyesters are thermally cross-linked by dicumyl peroxide. The thermal and mechanical properties of the cured PBSIs are extensively investigated.

### 3.2 Experimental Section

#### 3.2.1 Chemicals

Lipase acrylic resin from *Candida antarctica* lipase b (CALB, in immobilized form as Novozym\textsuperscript{®} 435, ≥ 5000 U/g), succinic acid (≥ 99 %), diethyl succinate (99 %), itaconic acid (≥ 99 %), dimethyl itaconate (99 %), 1,4-butanediol (≥ 99 %), cyclohexane (≥ 99 %, anhydrous), hexane (≥ 99 %), toluene (99.8 %, anhydrous), diphenyl ether (99 %), chloroform, and dicumyl peroxide (98 %) were purchased from Sigma-Aldrich. 1,4-Benzquinone (≥ 98 %) was ordered from TCI Europe. CALB was pre-dried in the presence of phosphorus pentoxide in a desiccator at room temperature under a high vacuum for 16 h. Diphenyl ether was dried with
calcium hydride and distilled under reduced pressure. All other chemicals were used as received.

3.2.2 General Procedure for CALB-Catalyzed Polymerization by Using Different Monomer Substrates and Polymerization Methods

3.2.2.1 General Procedure for CALB-Catalyzed Polycondensation of Succinate, Itaconate and 1,4-Butanediol in Bulk via a Two-Stage Method

We followed the similar procedure as reported in literature to perform a two-stage enzymatic polymerization. Succinate (10 mmol), itaconate (10 mmol), 1,4-butanediol (20 mmol), and pre-dried CALB (10 wt % in relation to the total amount of monomers) were added into a 25 mL flask. The reactants were magnetically stirred at 80 °C in an oil bath for 2 h under the protection of nitrogen. After that, the reaction pressure was reduced to 2 mmHg and the reaction temperature was maintained at 80 °C. The total polymerization lasted for 96 h.

Chloroform was introduced to terminate the enzymatic polycondensation. CALB was filtered off and washed with a small amount of chloroform three times. The solutions were then combined, condensed and poured into cold methanol (or hexane) for precipitation. The precipitates were collected and washed with methanol (or hexane) three times. Finally, the obtained polyesters were dried in a vacuum oven at 20 - 40 °C for 2 - 3 days, and then stored at room temperature in vacuo before analysis.

3.2.2.2 General Procedure for CALB-Catalyzed Polycondensation of Succinate, Itaconate and 1,4-Butanediol in Diphenyl Ether via a Two-Stage Method

Succinate (5.55 mmol), itaconate (5.55 mmol), 1,4-butanediol (11.10 mmol) and diphenyl ether (150 wt %) were added into a round-bottom flask with pre-dried CALB (10 wt %). The remaining procedure was the same as described in 3.2.2.1.

3.2.2.3 General Procedure for CALB-Catalyzed Azeotropic Polycondensation of Succinate, Itaconate and 1,4-Butanediol in the Mixture of Cyclohexane and Toluene

The following procedure was performed for the enzymatic polymerization by azeotropic distillation as reported in literature. Succinate (5 mmol), itaconate (5 mmol), 1,4-butanediol (10 mmol), cyclohexane (60 mL) and toluene (10 mL)
were introduced into a 100 mL three-necked round-bottom flask with pre-dried CALB (10 wt %). A Dean-Stark apparatus filled with 5 g of activated 4 Å molecular sieves was attached to one neck of the flask. The molecular sieves were replaced every 24 h. A tiny nitrogen flow was applied to another neck to promote the solvent evaporation. The reactants were magnetically stirred, and the polycondensation temperature was set to 80 °C at which the stable azeotropic distillation took place. During the polymerization, 5 mL of the mixture of cyclohexane and toluene (6:1, v/v) was added into the reaction every 24 h to compensate the solvent loss; and insoluble products were formed and adhered to the flask after 2 days reaction. The total polymerization time was 168 h.

CALB was filtered off after the polymerization. Chloroform was introduced to the reaction flask to dissolve the products. The flask and the filter paper were washed three times by chloroform. Then the solutions were combined and condensed. The purification procedure was the same as described in 3.2.2.1.

3.2.3 Instrumental Methods

$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H homonuclear (COSY), and $^1$H-$^{13}$C heteronuclear single quantum coherence (HSQC) spectra were recorded on a Varian VXR spectrometer (400 MHz for $^1$H-NMR and 100 MHz for $^{13}$C-NMR analysis). Samples were dissolved in CDCl$_3$-$d_1$. The reported chemical shifts were referenced to the resonances of CDCl$_3$-$d_1$. The number average molecular weights ($\overline{M}_n$) and the molar compositions of the obtained polyesters were determined by $^1$H-NMR according to the method established in our previous report.$^{38}$

Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a Bruker IFS88 FT-IR spectrometer. For each sample, 128 scans were performed.

The number average molecular weights ($\overline{M}_n$), weight average molecular weights ($\overline{M}_w$), and dispersity ($D$, $\overline{M}_w/\overline{M}_n$) were measured by Size Exclusion Chromatography (SEC) using a Viscotek SEC equipped with a triple detector at 30 °C. Chloroform (HPLC grade) was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights were calculated based on the universal calibration method, using the calibration curve generated from narrow dispersity polystyrene standards (Agilent and Polymer Laboratories, $\overline{M}_w$’s ranging from 645 to 3001000 g/mol).

The glass transition temperatures ($T_g$) and melting temperatures ($T_m$) were measured by Differential Scanning Calorimetry (DSC) using a TA-Instruments Q1000 DSC. The heating and cooling rate were 10 °C/min.
Wide-angle X-ray Diffraction (WAXD) was performed on a Bruker D8 Advance diffractometer at room temperature. The degree of crystallinity ($\chi_c$) was determined using the method reported in literature.$^{27,50,51}$

### 3.2.4 $^1$H- and $^{13}$C-NMR Analysis of the Obtained Poly(butylene succinate), Poly(butylene succinate-co-itaconate)s, and Oligo(butylene itaconate)

#### Poly(butylene succinate) (PBS) $^1$H-NMR (400 MHz, CDCl$_3$-$d_1$, $\delta$): 4.02 - 4.18 (m, 4H, -CO-O-$CH_2$-, from 1,4-butanediol), 2.54 - 2.65 (m, 4H, -OC-$CH_2$-, from succinate), 1.54 - 1.94 (m, 4H, -$CH_2$-, from 1,4-butanediol); low intensity resonances ascribed to the protons from the end groups: 3.60 - 3.68 (m, -$CH_2$-OH, from 1,4-butanediol) and 1.20 - 1.27 (m, -OCH$_2$CH$_3$, from succinate). $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, $\delta$): 172.4 ($-CO-$, from itaconate), 133.8 ($-CO-O-$, from itaconate), 165.0 - 167.1 ($-C=C-$, from itaconate), 128.2 ($-C=CH_2$-, from itaconate), 64.0 - 64.7 ($-CO-$, from 1,4-butanediol); low intensity signals assigned to the carbons from the end groups: 64.5 ($-CH_2CH_2CH_2CH_2OH$), 25.1 ($-CH_2$-, from 1,4-butanediol), 29.0 ($-CH_2$-, from succinate), 25.2 ($-CH_2$-, from 1,4-butanediol); low intensity signals assigned to the carbons from the end groups were determined at 64.6 - 64.8 ($-CH_2CH_2CH_2CH_2OH$), 62.0 ($-CH_2CH_2CH_2CH_2OH$), 25.0 ($-CH_2CH_2CH_2CH_2OH$), and 14.2 ($-OCH_2$CH$_3$).

#### Poly(butylene succinate-co-itaconate) (PBSIs) $^1$H-NMR (400 MHz, CDCl$_3$-$d_1$, $\delta$): 6.30 (s, 1H, H-CH=C- from itaconate), 5.70 (s, 1H, H-$CH=CH_2$- from itaconate), 4.06 - 4.21 (m, 4H, -CO-O-$CH_2$-, from 1,4-butanediol), 3.31 (s, 2H, -$CH_2$-CO-, from itaconate), 2.50 - 2.70 (m, 4H, -OC-$CH_2$-, from succinate), 1.60 - 1.78 (m, 4H, -$CH_2$-, from 1,4-butanediol); low intensity resonances ascribed to the protons from the end groups: 3.75 (s, -O-$CH_3$, from itaconate), 3.63–3.73 (m, -$CH_2$-OH, from 1,4-butanediol) and 1.15 - 1.32 (m, -OCH$_2$CH$_3$, from succinate). $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, $\delta$): 172.2 (-CO-, from succinate), 165.9 (-C=C- CO-O-, from itaconate), 133.8 (-$C=CH_2$, from itaconate), 128.2 (-$C=CH_2$, from itaconate), 62.5 - 65.0 (-CO-O-$CH_2$-, from 1,4-butanediol), 37.6 (-$CH_2$-, from itaconate), 29.1 (-$CH_2$-, from succinate), 25.1 (-$CH_2$-, from 1,4-butanediol); low intensity signals assigned to the carbons from the end groups were determined at 64.6 - 64.8 (-$CH_2CH_2CH_2CH_2OH$), 62.0 (-$CH_2CH_2CH_2CH_2OH$), 60.6 (-$OCH_2$CH$_3$), 29.0 (-$CH_2CH_2CH_2CH_2OH$), 25.0 (-$CH_2CH_2CH_2CH_2OH$), and 51.7 - 52.1 (-$CH_3$, from itaconate).

#### Oligo(butylene itaconate) (OBI) $^1$H-NMR (400 MHz, CDCl$_3$-$d_1$, $\delta$): 6.30 (s, 1H, H-CH=C- from itaconate), 5.70 (s, 1H, H-$CH=CH_2$- from itaconate), 3.94 - 4.31 (m, 4H, -CO-O-$CH_2$-, from 1,4-butanediol), 3.31 (s, 2H, -$CH_2$-CO-, from itaconate), 1.48 - 2.00 (m, 4H, -$CH_2$-, from 1,4-butanediol); low intensity resonances assigned to the protons from the end groups: 3.75 (s, -O-$CH_3$, from itaconate), and 3.60 - 3.70 (m, -$CH_2$-OH, from 1,4-butanediol). $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, $\delta$):
170.6 (-CO-, from itaconate), 165.0 - 167.1 (-C=CO-O-, from itaconate), 133.6 (-C=CH2, from itaconate), 128.4 (-C=CH2, from itaconate), 64.0 - 64.7 (-CO-CH2-, from 1,4-butanediol), 37.9 (-CH2-, from itaconate), 25.1 (-CH2-, from 1,4-butanediol); signals assigned to the carbons from the end groups were determined at 64.7 - 65.1 (-CH2CH2CH2CH2OH), 62.2 (-CH2-, from itaconate), 51.8 (-CH3, from itaconate), and 29.1 (-CH2CH2CH2CH2OH).

3.2.5 ATR-FTIR Analysis of Poly(butylene succinate), Poly(butylene succinate-co-itaconate)s, and Oligo(butylene itaconate)

The overlay ATR-FTIR spectra of PBS, PBSIs and OBI are shown in Figure 3.1. The IR absorption bands were assigned as follows.

**ATR-FTIR** (cm⁻¹): 2800 - 3000 (-CH- stretching vibrations), 1710 (-C=O stretching vibrations), 1636 (asymmetric -C=C- stretching vibrations), 1310 - 1470 (multi-bands, -CH2- deformation vibrations), 1185 (asymmetric -C-O-C- stretching vibrations), 1150 (-C-O-C- symmetric stretching vibrations), 998 (=C-H, out-of-plane deformation vibrations), 926 (-CO-C=CH2 out-of-plane deformation vibrations), 805 - 815 (-CH2- rocking vibrations, -C=CH2 twisting vibrations), 740 - 750 (-CH2-) rocking vibrations).

![Figure 3.1. ATR-FTIR spectra of poly(butylene succinate), poly(butylene succinate-co-itaconate)s and oligo(butylene itaconate).](image)

**Figure 3.1.** ATR-FTIR spectra of poly(butylene succinate), poly(butylene succinate-co-itaconate)s and oligo(butylene itaconate).

3.2.6 Cross-linking of Poly(butylene succinate-co-itaconate)s and their Mechanical Properties Characterizations

PBSI (1 g) was mixed with dicumyl peroxide (25 mg). The mixtures were then ground, where after filled into a steel mold and thermally cross-linked at 150 °C for
30 min by hot-pressing under the pressure of 2.7 MPa. The resulting bars (55mm × 5.6mm × 0.5mm) were transparent.

Tensile tests were performed on an Instron 5565 Series Universal Testing Instrument at room temperature. The crosshead speed was 10 mm/min.

3.3 Results and Discussion

3.3.1 CALB-Catalyzed Dehydration Polycondensation of Succinic Acid, Itaconic Acid and 1,4-Butanediol via Different Polymerization Methods

Succinic acid, itaconic acid and 1,4-butanediol are commercially available biobased monomers. They are good and cheap renewable building blocks for polyester synthesis. In this study, they were enzymatically polycondensed by CALB via different polymerization methods. The results are summarized in Table 3.1.

Table 3.1. The CALB-catalyzed dehydration polycondensation of succinic acid, itaconic acid and 1,4-butenediols via different polymerization methods

<table>
<thead>
<tr>
<th>Polymerization method</th>
<th>Solvent</th>
<th>Molar composition (Feed F&lt;sub&gt;s&lt;/sub&gt;, F&lt;sub&gt;i&lt;/sub&gt;, F&lt;sub&gt;b&lt;/sub&gt;, X&lt;sub&gt;s&lt;/sub&gt;, X&lt;sub&gt;i&lt;/sub&gt;, X&lt;sub&gt;b&lt;/sub&gt;)</th>
<th>Molecular weight (M&lt;sub&gt;n&lt;/sub&gt;, M&lt;sub&gt;o&lt;/sub&gt;, M&lt;sub&gt;w&lt;/sub&gt;, D)</th>
<th>Yield (%)</th>
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<tr>
<td>Two-stage melt</td>
<td>None</td>
<td>Feed: 50:0:50 50:0 50:0 50:0</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;: 1.4; M&lt;sub&gt;o&lt;/sub&gt;: 2.3; M&lt;sub&gt;w&lt;/sub&gt;: 3.0; D: 1.3</td>
<td>78</td>
</tr>
<tr>
<td>polymerization</td>
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<td>PBSI: 50:50:50:31:26:43</td>
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<tr>
<td>Azeotropic</td>
<td>Cyclohexane (6) Toluene (1)</td>
<td>Feed: 50:0:50:50:0:50</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;: 0.9; M&lt;sub&gt;o&lt;/sub&gt;: 1.6; M&lt;sub&gt;w&lt;/sub&gt;: 2.2; D: 1.4</td>
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<tr>
<td>Two-stage solution</td>
<td>Diphenyl ether</td>
<td>Feed: 50:0:50:50:54:0 46</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;: 0.5; M&lt;sub&gt;o&lt;/sub&gt;: 0.6; M&lt;sub&gt;w&lt;/sub&gt;: 1.1; D: 1.8</td>
<td>27</td>
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<tr>
<td>polymerization</td>
<td></td>
<td>PBSI: 25:25:50:35:15:50</td>
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</table>

<sup>a</sup> F<sub>s</sub>, F<sub>i</sub>, F<sub>b</sub> represent the molar feed ratio of succinic acid, itaconic acid, and 1,4-butanediol, respectively; <sup>b</sup> X<sub>s</sub>, X<sub>i</sub>, X<sub>b</sub> represent the molar percentage of succinate, itaconate and butylene segments in the obtained poly(butylene succinate-co-itaconate) (PBSIs), respectively, which were determined by 1H-NMR; <sup>c</sup> The number average molecular weight (M<sub>n</sub>, kg/mol) was calculated from 1H-NMR; <sup>d</sup> The number average molecular weight (M<sub>n</sub>, kg/mol), weight average molecular weight (M<sub>w</sub>, kg/mol), and dispersity (D, M<sub>w</sub>/M<sub>n</sub>) were determined by SEC in chloroform; <sup>e</sup> Isolated yield (%); <sup>f</sup> The reaction yield and the SEC data were determined by using unpurified products; <sup>g</sup> The reaction gelated during the polycondensation; <sup>h</sup> The obtained products partially gelated at 40 °C in the vacuum oven; <sup>i</sup> The obtained products were purified in hexane.

The major problem of using unactivated dicarboxylic acids having short-chain lengths in enzymatic polymerization is the phase separation, which is caused by
their poor solubility in the reaction media and their relatively high melting temperatures (\(T_m\)’s).\textsuperscript{26,38} In our study, succinic acid and itaconic acid have a rather low solubility in 1,4-butanol and in the tested solvents. Furthermore, their \(T_m\)’s, which are 184 and 162 - 164 °C, respectively, are much higher than the applied reaction temperature (80 °C). Therefore, the enzymatic polymerization with succinic acid and itaconic acid were heterogeneous. In this case, the biocatalytic efficiency was quite low since the accessibility of the dicarboxylic acids to the enzyme CALB was limited. As a result, only low molecular weight products were obtained, with the \(M_n\)’s of around 0.4 - 2.3 kg/mol.

From Table 3.1 we can also conclude that the two-stage enzymatic melt polymerization and the enzymatic azeotropic polymerization are more suitable for the dehydration polycondensation of succinic acid, itaconic acid and 1,4-butanol. In bulk polymerization, all reactants are confined in a high concentration state, in which the collision probability of the reactants with CALB increases. Therefore, the dicarboxylic acids gain more chances to access the active site of CALB. On the other hand, in the azeotropic polymerization with an excess amount of cyclohexane and toluene, the dicarboxylic acids may be slightly better dissolved; therefore their reactivity with CALB is enhanced. As a result, oligomers are produced with desired molar compositions, longer chains, and better reaction yields by using these two methods.

### 3.3.2. CALB-Catalyzed Polycondensation of Diethyl Succinate, Dimethyl Itaconate and 1,4-Butanediol via Different Polymerization Methods

Homogeneous reactions were obtained when the unactivated dicarboxylic acids were replaced with their alkyl diester derivatives. Besides, we noticed that the carbon-carbon double bonds tended to be cross-linked during the melt and azeotropic polymerization when the itaconate feed ratio was more than 25 mol %. To avoid gelation, 1,4-benzoquinone (0.1 %, w/w) was introduced into the melt and azeotropic polymerization when the feed ratio of itaconate was equal to or higher than 25 mol %.

By altering the feed composition and applying different polymerization methods, polyesters with different chemical compositions and molecular weights were successfully produced, as summarized in Table 3.2.
3.3.2.1 Chemical Structures of the Obtained Poly(butylene succinate), Poly(butylene succinate-co-itaconate)s and Oligo(butylene itaconate)

The chemical structures of the obtained polyesters were characterized by NMR and ATR-FTIR spectrometry. Both $^1$H-NMR, $^{13}$C-NMR and ATR-FTIR analysis confirmed the chemical structures and compositions of PBS, PBSIs and OBI (Figures 3.1-3.3).

**Table 3.2.** The CALB-catalyzed polycondensation of diethyl succinate, dimethyl itaconate and 1,4-butanediol via different polymerization methods

<table>
<thead>
<tr>
<th>Polymerization method</th>
<th>Solvent</th>
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<th>Molar composition</th>
<th>Molecular weight</th>
<th>Yield $^c$</th>
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</table>

$^a$ $F_S$, $F_I$, $F_B$ represent the molar feed ratio of succinic acid, itaconic acid, and 1,4-butanediol, respectively; $^b$ $X_S$, $X_I$, $X_B$ represent the molar percentage of succinate, itaconate and butylene segments in the obtained poly(butylene succinate-co-itaconate)s (PBSIs), respectively, which were determined by $^1$H-NMR; $^c$ The number average molecular weight ($M_n$, kg/mol) was calculated from $^1$H-NMR; $^d$ The number average molecular weight ($M_w$, kg/mol) and dispersity ($D, M_w/M_n$) were determined by SEC in chloroform; $^e$ Isolated yield (%); $^f$ The products were precipitated in cold methanol (-20 °C); $^g$ The products were precipitated in hexane (r.t.); $^h$ The unpurified products were dried in a vacuum oven and used for the SEC measurement; $^i$ No products were obtained by using cold methanol (-20 °C), so the products were precipitated in hexane (r.t.). $^{1,4}$-Benzoquinone (0.1 %, w/w, radical inhibitor) was introduced to the polycondensation to prevent gelation.

The presence of the following resonances in the $^1$H-NMR spectra (Figure 3.2) did prove the successfully incorporation of itaconate moieties into the co-polyesters, including the two singlet peaks assigned to vinyl protons at around 6.3 ppm and 5.7 ppm, the resonance belonging to the methylene protons of itaconate at around 3.3 ppm, and the broad peaks at around 4.2 ppm ascribed to butylene protons that are
directly linked to itaconate. Moreover, in the $^{13}$C-NMR spectra (Figure 3.3), the split of carbonyl signals at around 164 ppm - 173 ppm, the appearance of the vinyl carbon peaks at around 134 ppm and 128 ppm, as well as, the rising of the resonances ascribed to the methylene carbons from itaconate at around 38 ppm, also confirmed the formation of PBSIs. The detailed NMR peak assignments are described in Section 3.2.4.$^{26, 35, 38}$

**Figure 3.2.** $^1$H-NMR spectra of the obtained polyesters.

**Figure 3.3.** $^{13}$C-NMR spectra of the obtained polyesters.

The NMR assignments are further supported by two-dimensional NMR spectroscopy, including $^1$H-$^1$H homonuclear (COSY) and $^1$H-$^{13}$C heteronuclear single quantum coherence (HSQC) spectroscopy, as illustrated in Figure 3.4 and Figure 3.5, respectively. Due to the spatial configuration of the vinyl group suspending to the main chain of PBSIs, the vinyl protons, H$_d$ and H$_e$, are coupled to each other; and correlated to the methylene protons H$_f$, even though they are three carbons apart. Therefore, the presence of the cross peaks H$_d$/H$_d$, H$_e$/H$_e$ and H$_e$/H$_d$ in
the COSY spectrum confirmed the existence of itaconate fragments in the tested PBSIs. In addition, the protons in the methylene groups that link directly to the ester bonds, H_b and H_b', displayed different resonances in the ^1H-NMR spectra since their adjacent dicarboxylic segments are different. They are coupled with the protons H_c from the same butylene segments. Moreover, the four methylene protons from succinate (H_a) do not show off-diagonal peaks since they are identical to each other and they are not coupled to the other protons in PBSIs. Therefore, their proton signals overlapped at around 2.5 - 2.7 ppm in the ^1H-NMR spectra.

\[ \text{Figure 3.4. } ^1\text{H-}^1\text{H homonuclear (COSY) spectrum of poly(butylene succinate-co-itaconate) containing around 35 mol % of itaconate units (PB_{50S_{16I_{34}}}).} \]

Moreover, the carbon peak at 128 ppm shows two cross peaks (H_d/C_g and H_e/C_g) with the two vinyl proton signals at 6.3 and 5.7 ppm, respectively, as shown in Figure 3.5. This confirms the preservation of the vinyl groups in the co-polyester. Meanwhile, the carbon peak at 38 ppm (C_f) corresponds to the proton singlet at 3.3 ppm (H_t). The cross peak H_t/C_f supports the NMR assignments of the methylene groups from itaconate. In addition, the carbon peak at 64 ppm (C_{bb&b'}) and the proton multiplet at around 4.1 ppm (H_b) and 4.2 ppm (H_b'), as well as, the carbon peak at 25 ppm (C_e) and the proton multiplet at around 1.7 ppm (H_c), correspond to the methylene groups from the butylene moieties. Moreover, the correlation signal C_v/H_a indicates the connectivity of the carbon peak at 29 ppm (C_v) with the broad
proton peak at around 2.6 ppm (H_a). They are assigned to the methylene groups from succinate.

The chemical structures of the obtained products were also characterized by ATR-FTIR spectrometry, as described in Section 3.2.5. The absorption band at around 1636 cm\(^{-1}\) is due to the asymmetric stretching vibrations of -C=\(\text{C}\)- groups from itaconate. It rises in intensity with increasing amount of itaconate in the unsaturated polyesters (see Figure 3.1).

Figure 3.5. \(^1\text{H}-^{13}\text{C}\) heteronuclear single quantum coherence (HSQC) spectrum of poly(butylene succinate-co-itaconate) containing around 35 mol % of itaconate units (PB\(_{50}\)S\(_{16}\)I\(_{34}\)).

3.3.2.2 Effect of Enzymatic Polymerization Method on the Molar Percentage of Itaconate

We have already reported that the two-stage enzymatic polymerization of diethyl succinate, dimethyl itaconate, and 1,4-butanediol in diphenyl ether yielded PBSIs with tunable molar percentage of itaconate from 0 to 24 %, by altering the molar feed ratio of itaconate from 0 to 25 %; and PBSIs containing only around 15 - 16 mol % of itaconate were produced if the molar feed ratio of itaconate was increased to 30 and 35 %. However, as shown in Figure 3.6, the enzymatic azeotrophic polymerization resulted in products with desirable molar compositions by adjusting the itaconate feed ratio from 0 to 50 mol %. Meanwhile, the itaconate content in
the unsaturated polyesters can be controlled from 0 to 34 mol % by using the two-stage enzymatic melt polymerization. In a word, in terms of biocatalytic synthesis of itaconate-based polyesters with controllable molar compositions, the azeotropic polymerization in the mixture of cyclohexane and toluene is the best choice; and the melt polymerization is better than the solution polymerization in diphenyl ether. Besides, the two-stage enzymatic polymerization in diphenyl ether resulted in PBSI with the least amount of itaconate, when the itaconate feed ratio was 35 mol %. This can be explained by the different microstructures formed in PBSI from different polymerization methods, as illustrated in our previous report, and in Section 3.3.3.

**Figure 3.6.** The molar percentage of itaconate in the obtained polyesters as a function of the feed ratio of itaconate (mol %).

### 3.3.2.3 Effect of Enzymatic Polymerization Method on Molecular Weights

Figure 3.7 depicts the product $M_n$ from different polymerization methods as a function of the feed ratio of itaconate. In general, first the $M_n$ increased as the itaconate feed ratio was increased, and then decreased. This tendency was observed in all the tested polymerization methods. The increase of the product $M_n$ with increasing amount of the added itaconate was due to the higher solubility of PBSIs in the reaction media and its lower melting temperature ($T_m$). For instance, the $M_n$ of the obtained PBS was relatively lower since it precipitated and crystallized fast from the reaction media due to its poor solubility and high $T_m$ (around 113 °C). However, the $T_m$ of the synthesized PBSIs decreased significantly with increasing amount of itaconate, for example, the $T_m$ of the tested PB$_{50}$S$_{35}$I$_{15}$ was around 80 °C. Therefore, the reaction with more than 10 mol % of itaconate maintained always at a homogenous state and PBSIs with higher molecular weights could be produced. However, the product $M_n$ decreased significantly when the itaconate feed ratio
exceeded 25 mol %. We thought that this is due to the relatively low enzymatic polymerizability of dimethyl itaconate, as illustrated in our previous report.\textsuperscript{38}

For the CALB-catalyzed polycondensation of diethyl succinate and 1,4-butanediol, the tested polymerization methods had no significant influence on the enzymatic polymerization. They yielded low molecular weight PBS with the $M_n$’s of 2.7 - 4.5 kg/mol. As the itaconate feed ratio reached to 15 and 25 mol %, the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene, as well as, the two-stage enzymatic polymerization in diphenyl ether, resulted in high molecular weight PBSIs, with the $M_n$’s of around 11.1 - 16.2 kg/mol. However, the product $M_n$ from the bulk polymerization with the same feed compositions was lower, between 6.9 - 8.4 kg/mol. We attributed this to the higher viscosity of the reaction media and the lower diffusion of the reactants in the melt polymerization. Moreover, if the itaconate feed ratio was increased to 35 mol %, the product $M_n$ from the azeotropic polymerization and the melt polymerization was 6.0 and 3.4 kg/mol, respectively. These values were clearly higher than that from the solution polymerization in diphenyl ether, which was only 0.5 kg/mol. Furthermore, for the CALB-catalyzed polycondensation of dimethyl itaconate and 1,4-butanediol, only oligomers were prepared, in spite of the different polymerization methods applied. The product $M_n$ was less than 1.0 kg/mol.

\textbf{Figure 3.7.} The number average molecular weight of the obtained polyesters ($M_n$, from SEC) against the feed ratio of itaconate (mol %).

From Table 3.2, and Figures 3.6 - 3.7, we can draw the conclusion that the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene is more reliable for producing high molecular weight polyesters with controllable molar compositions and, therefore, it is the best method for the enzymatic synthesis of PBSIs. In addition, the two-stage enzymatic polymerization in diphenyl ether is suitable for preparing high molecular weight PBSIs with less than or equal to 25
mol % of itaconate. Moreover, low molecular weight PBSIs with tunable molar compositions can be obtained by using the two-stage enzymatic melt polymerization.

The effects of the tested polymerization method on the enzymatic synthesis of PBSI can be explained by the different microstructures produced by CALB, as illustrated in Section 3.3.3 (see below).

### 3.3.3 Microstructures of Poly(butylene succinate-co-itaconate)s from Different Polymerization Methods

As suggested in our previous report, there are six possible microstructures in PBSIs, as shown in Figure 3.8. These microstructures can be classified into three groups according to the distance between the vinyl group and the butylene moiety. First, the microstructures of S-B-S, S-B-I-1 and I-B-I-1 are similar since the double bonds are at least four atoms away from the butylene carbons marked as C-1, C-2, and C-3, respectively. Second, the microstructures of S-B-I-2 and I-B-I-2 are comparable, because the butylene carbon marked as C-4 or C-5 is three atoms away from the vinyl group. Third, the carbons marked as C-6 in the microstructure of I-B-I-3 are unique, as there are two vinyl groups close to the butylene segment.

![Figure 3.8](image)

Figure 3.8. Six possible microstructures in poly(butylene succinate-co-itaconate)s.

These three kinds of carbons can be distinguished by $^{13}$C-NMR. As presented in Figure 3.9, the singlet resonance assigned to the microstructures of S-B-S, S-B-I-1 and I-B-I-1 in PBSIs is at around 64.10 ppm, which is a bit higher than that of PBS at 63.81 ppm. Meanwhile, the two single peaks at around 64.30 ppm and 64.40 ppm are ascribed to the microstructures of S-B-I-2 and I-B-I-2. In addition, the broad peaks assigned to the microstructure of I-B-I-3 are between 64.51 ppm to 64.66 ppm. Besides, the other broad peaks between 64.67 ppm to 64.94 ppm are assigned to the methylene carbons from the butylene end groups.
Due to the hindrance effects of the two carbon-carbon bonds, the formation of I-B-I-3 is the most difficult, compared to the other microstructures. However, trimers with the I-B-I-3 microstructures are favored by the enzyme CALB, as the remaining two ester bonds are no longer hindered by the vinyl groups. Therefore, the reactivity of these trimers can be even higher than that of diethyl succinate since they are terminated by two methoxy groups. This is due to the fact that methyl esters are normally chemically much more reactive than ethyl esters. As a result, the production of I-B-I-3 microstructures will facilitate the chain growth of PBSIs. However, as shown in Figure 3.9, the I-B-I-3 microstructures were only identified in PB_{50}S_{25}I_{25} produced from the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene; but they were not detected in the tested PBSIs produced from the enzymatic polymerization in bulk and in diphenyl ether. This explained why the enzymatic azeotropic polymerization in the mixture of cyclohexane and toluene yielded PB_{50}S_{25}I_{25} with the highest molecular weight when the molar feed ratio of diethyl succinate, dimethyl itaconate and 1,4-butane diol was 25:25:50.

**Figure 3.9.** Microstructures of poly(butylene succinate-co-itaconate)s produced from different polymerization method. For the synthesis of poly(butylene succinate-co-itaconate)s containing around 25 mol % of itaconate, the molar feed ratio of diethyl succinate, dimethyl itaconate and 1,4-butane diol was 25:25:50.

As the molar feed composition of diethyl succinate, dimethyl itaconate and 1,4-butane diol was changed to 15:35:50, I-B-I-3 microstructures were present also in PB_{50}S_{16}I_{34} produced from the enzymatic azeotropic polymerization (Figure 3.10), and they were also identified in the co-polymers synthesized from the enzymatic melt polymerization but the corresponding carbon resonances possessed a rather...
low intensity. This indicated that only trace amount of I-B-I-3 microstructures were produced by CALB in PB$_{50}$S$_{16}$I$_{34}$ using the enzymatic melt polymerization. Therefore, the product $M_n$ from the enzymatic melt polymerization was lower than that from the enzymatic azeotropic polymerization.

**Figure 3.10.** Microstructures of poly(butylene succinate-co-itaconate)s from different polymerization methods. For the synthesis of poly(butylene succinate-co-itaconate)s containing around 35 mol% of itaconate, the molar feed ratio of diethyl succinate, dimethyl itaconate and 1,4-butandiol was 15:35:50.

In conclusion, the effects of polymerization methods on the enzymatic polycondensation of diethyl succinate, dimethyl itaconate and 1,4-butandiol can be explained by the different microstructures formed in the co-polysters. We found that CALB is capable of producing I-B-I-3 microstructures in the mixture of cyclohexane and toluene by azeotropic distillation or in bulk under reduced pressure. However, this capability is limited in the enzymatic melt polymerization since the esterification reactions are insufficient and quite slow. This is due to the high viscosity of the reaction media and the low diffusion of the reactants under melt conditions. Moreover, the absence of I-B-I-3 microstructures in PBSIs synthesized from the two-stage enzymatic polymerization in diphenyl ether is probably due to the frequently occurrence of the intermolecular esterifications between polyester chains. As a result, the I-B-I-3 microstructures are converted to the other easier formed microstructures, like I-B-I-1, I-B-I-2 and S-B-I-1. However, during the enzymatic azeotropic polymerization, the intermolecular esterification is prevented in the mixture of cyclohexane and toluene since the concentration of the reactants is quite low.
### 3.3.4 Crystalline Properties of the Obtained Polyesters

The amount of itaconate has obvious effects on the WAXD patterns of the obtained polyesters. We found that the WAXD pattern of the tested PBSIs changed from PBS-based to poly(butylene itaconate) (PBI)-based, when more itaconate is incorporated; and this change occurred when the molar percentage of itaconate amounted to 25%. As presented in Figure 3.11, characteristic reflection peaks at 19.7, 21.8 (shoulder peak), and 22.6 ° were observed in the WAXD spectrum of the tested PBS, and the WAXD pattern of PB_{50S_{55}I_{34}} was almost the same as that of PBS. However, the tested PB_{50S_{16}I_{34}} exhibited a totally different WAXD pattern, which showed only two sharp reflection peaks at 20.0 and 20.6 ° respectively. This suggested that new crystal structures are formed due to the ordered chain packing of itaconate-butylene-itaconate segments. Meanwhile, five reflection peaks were observed in the WAXD spectrum of the obtained PB_{50S_{25}I_{25}}. Three of them can be assigned to the WAXD pattern of PBS and the other two are identical to the WAXD pattern of the tested PB_{50S_{16}I_{34}}. This indicated that both PBS-based crystal structures and PBI-based crystal structures are present in PB_{50S_{25}I_{25}}. Furthermore, a broad amorphous halo appeared in the WAXD spectrum of the tested oligo(butylene itaconate) (OB_{47I_{53}}) because this oil-like oligomer had a rather low molecular weight and no crystallinity.

![WAXD spectra](image)

**Figure 3.11.** WAXD spectra of the tested poly(butylene succinate), poly(butylene succinate-co-itaconate)s and oligo(butylene itaconate).

The degree of crystallinity ($\chi_c$) and melt enthalpy ($\Delta H_m$) of the obtained polyesters are also affected by the itaconate content. As illustrated in Figure 3.12, the $\chi_c$ of the tested PBSI reduced from 69 to 31 % as the molar percentage of itaconate increased from 0 to 25 %. This can be explained by the reduction of chain regularity by incorporation of different microstructures into the tested PBSI. We
thought that the unsaturated polyester chain becomes more irregular with increasing amount of S-B-I, 1-B-I-1 and 1-B-I-2 microstructures; therefore the ordered chain packing is greatly hindered and the degree of crystallinity decreases accordingly. However, the $\chi_c$ increased to 63 % when the molar percentage of itaconate in the tested PBSI further reached 34 %. In this case, the crystallization is dominated by the chain packing of itaconate-butylene-itaconate segments rather than by succinate-butylene-succinate or succinate-butylene-itaconate moieties. Therefore, the polyester chain becomes more regular and this enhances the crystallization ability of the obtained PB$50S_{16}I_{34}$. Moreover, the $\Delta H_m$ showed the same trend as the degree of crystallinity. The $\Delta H_m$ decreased first from 91 to 30 J/g as the molar percentage of itaconate in the tested PBSI was increased from 0 to 25 %; then, it slightly added up to 38 J/g when the molar percentage of itaconate was further increased to 34 %.

![Figure 3.12.](image)

**Figure 3.12.** Degree of crystallinity ($\chi_c$) and melt enthalpy ($\Delta H_m$) of the obtained polyesters as a function of the molar percentage of itaconate. The $\chi_c$ values were calculated from WAXD and the $\Delta H_m$ values were determined from the first DSC heating curves.

We also noticed that the melting temperature ($T_m$, from the first DSC heating curve) of the tested PBSI with 34 mol % of itaconate is the lowest among all the tested polyesters, even though its degree of crystallinity is the second highest. This is due to the fact that the close packing capability are greatly decreased by the highest amount of the pendant carbon-carbon bonds in PB$50S_{16}I_{34}$.

### 3.3.5 Thermal and Mechanical Properties of the Cross-Linked Poly(butylene succinate-co-itaconate)s

The obtained unsaturated polyesters were thermally cured at 150 °C in the presence of dicumyl peroxide. We found that all carbon-carbon double bonds were fully consumed. As confirmed by ATR-FTIR (see Figure 3.13), the characteristic
absorption band ascribed to the -C=O stretching vibrations at around 1636 cm\(^{-1}\) disappeared completely in the ATR-FTIR spectrum of the cured PBSI.

**Figure 3.13.** Representative ATR-FTIR spectra of poly(butylene succinate-co-itaconate) containing around 25 mol% of itaconate (PB\(_{50}S_{25}I_{25}\)) before and after cross-linking.

The thermal properties of the untreated PBSIs and the cross-linked PBSIs were characterized by DSC. As shown in Table 3.3, and Figure 3.14, the untreated PBSIs possess similar glass transition temperatures (T\(_g\)) at around \(-40^\circ\)C, which can be explained by the highly flexibility and mobility of the linear aliphatic polyester chains with or without the side carbon-carbon double bonds. Meanwhile, melting peaks were observed in the first heating curves of all the untreated PBSIs.

**Table 3.3.** Glass transition temperatures (T\(_g\)) and melting temperatures (T\(_m\)) of poly(butylene succinate) (PB\(_{50}S_{50}\)) and poly(butylene succinate-co-itaconate)s before and after cross-linking.
modulus and the ultimate tensile stress of the cured PB 50S40I10 are higher than that of the cured PB 49S35I16 since the residual crystals in the tested PB 49S35I16 enhanced the mechanical properties. As the concentration of the cross-linking moiety increases from 15 to 34 mol %, the Young’s modulus and the ultimate tensile stress increased from 11.58 ± 1.36 to 66.58 ± 6.96 MPa, 2.85 ± 0.60 to 10.34 ± 1.18 MPa, and 26 ± 4 to 28 ± 4%, respectively. These results are in accordance with other cured unsaturated polyesters as reported in literature.

However, the cross-linked PBSIs displayed different glass transitions and thermal transitions. For the tested PB50S40I10, there is a small increase in Tg after cross-linking, which is only 5 °C. This is due to the low concentration of the cross-linking moiety. In addition, melting peaks were still observed in the first and second DSC heating curves of the cured PB50S40I10; but the corresponding melting temperatures (Tm) decreases around 20 °C. This suggested that succinate-butylene-succinate segments can be partially crystallized in the confined network with a lower cross-linking density. Moreover, for the tested cured PBSIs with more than 10 mol % of itaconate, the Tg increases more than 12 °C and the melting transitions disappeared. This indicated that 15 mol % of itaconate is sufficient enough to form a fully cross-linked network, in which the crystallization of polyester chains is completely prevented. Meanwhile, we found that the more itaconate incorporated in PBSIs, the more the Tg increases after curing. This is due to the lower flexibility and mobility of the polyester chains which is caused by the higher cross-linking density.

The cured polyesters are brittle polymers. As shown in Table 3.4, the Young’s modulus, ultimate tensile stress, and rupture strain of the tested cross-linked PBSIs are around 11 - 66 MPa, 3 - 12 MPa, and 26 – 34 % respectively. The Young’s modulus and the ultimate tensile stress of the cured PB50S40I10 are higher than that of the cured PB49S35I16 since the residual crystals in the tested PB49S35I16 enhanced the mechanical properties. As the concentration of the cross-linking moiety increases from 15 to 34 mol %, the Young’s modulus and the ultimate tensile stress
of the cured PBSIs also increases. This is due to the higher cross-linking density in the cured polyesters. In conclusion, general speaking, the mechanical properties of the cross-linked PBSIs are in accordance with other cured unsaturated polyesters as reported in literature. 35

Table 3.4. Mechanical properties of the cross-linked poly(butylene succinate-co-itaconate)s

<table>
<thead>
<tr>
<th>Co-polyester</th>
<th>Young’s modulus (MPa)</th>
<th>Ultimate tensile stress (MPa)</th>
<th>Rupture strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB50S40I10</td>
<td>66.58 ± 6.96</td>
<td>10.34 ± 1.18</td>
<td>26 ± 4</td>
</tr>
<tr>
<td>PB49S35I16</td>
<td>11.58 ± 1.36</td>
<td>2.85 ± 0.60</td>
<td>34 ± 7</td>
</tr>
<tr>
<td>PB50S25I25</td>
<td>44.70 ± 16.08</td>
<td>6.99 ±3.02</td>
<td>30 ± 9</td>
</tr>
<tr>
<td>PB50S10I34</td>
<td>64.89 ± 13.23</td>
<td>11.73 ± 6.14</td>
<td>28 ± 4</td>
</tr>
</tbody>
</table>

3.4 Conclusions

Fully biobased saturated and unsaturated aliphatic polyesters and oligoesters are successfully produced by the CALB-catalyzed polycondensation of succinate, itaconate and 1,4-butanediol. By varying the feed ratio of itaconate and changing the polymerization method, high molecular weight PBSIs with tunable molar compositions are produced.

The enzymatic copolymerization of succinic acid, itaconic acid and 1,4-butanediol results in oligomers since the reactions with the unactivated dicarboxylic acids are heterogeneous.

By replacing the unactivated dicarboxylic acids with the alkyl diester derivatives, itaconate-based unsaturated polyesters are obtained, with relatively higher molecular weights. We found that the applied enzymatic polymerization method has significant effects on the molar compositions and molecular weights of the obtained polyesters. Among the tested methods, the azeotropic polymerization in the mixture of cyclohexane and toluene is the most suitable approach to synthesize high molecular weight PBSIs with desirable chemical compositions. In addition, the two-stage enzymatic polymerization in diphenyl ether is capable of producing high molecular weight PBSIs with less than 30 mol % of itaconate. Moreover, the two-stage enzymatic melt polymerization yields low molecular weight PBSIs with controllable chemical compositions.

13C-NMR study confirms that different microstructures are present in PBSIs produced by using different polymerization methods. We found that the formation
of I-B-I-3 microstructures \( \text{[structure]} \) is crucial for producing high molecular weight PBSIs with desired chemical compositions. We suggest that the occurrence of the intermolecular esterification leads to the absence of this microstructure.

The tested PBS and PBSIs are semi-crystalline polymers. The WAXD pattern, degree of crystallinity, and melt enthalpy of the obtained polyesters are greatly influenced by the amount of itaconate incorporated into the polyester chains.

The itaconate-based unsaturated polyesters are successfully thermally cross-linked in the presence of dicumyl peroxide. The \( T_g \) of the cured PBSI increases significantly with increase of cross-linking density. Moreover, the cured unsaturated polyesters are brittle materials, which possesses the Young’s modulus, ultimate tensile stress, and rupture strain of 11 - 66 MPa, 3 - 12 MPa, and 26 - 34 %, respectively.

### 3.5 Reference


Chapter 4

Environmentally Benign Synthesis of Saturated and Unsaturated Aliphatic Polyesters via Enzymatic Polymerization of Biobased Monomers

Abstract:
Aliphatic polyesters are of great interest due to their broad potential applications and sustainability. Itaconate-based aliphatic polyesters are even more appealing in biomedical and pharmaceutical fields, as they are renewable functional polymers that can be biodegradable, biocompatible, photo-curable, and might be bioresorbable. Herein, various biobased saturated aliphatic polyesters and itaconate-based unsaturated aliphatic polyesters are successfully produced via Candida antarctica lipase b (CALB)-catalyzed polycondensation of (potentially) biobased dimethyl itaconate, 1,4-butanediol and various diacid ethyl esters, using a two-stage method in diphenyl ether. The synthetic aliphatic polyesters reach high (weight average molecular weight) values up to 94 kg/mol. Studies on the effect of diacid ethyl esters on the enzymatic polymerization reveal that CALB prefers diacid ethyl esters having a chain length of more than 2 (n > 2, n is the number of methylene groups between the two carbonyl groups); and CALB shows the highest specificity for diethyl adipate among the tested diacid ethyl esters (n = 2 - 10). Moreover, the structure-property relationsips are discussed by investigating the chemical structures, crystalline properties and thermal properties of the obtained aliphatic polyesters, as well as, the thermal transitions and mechanical properties of the UV cross-linked unsaturated polyesters.

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