Chapter 5

Enzymatic Synthesis of Renewable 2,5-Bis(hydroxymethyl)furan-Based Polyesters

**Abstract:** 2,5-Bis(hydroxymethyl)furan (BHMF) is a highly valuable biobased rigid diol resembling aromatic monomers in polyester synthesis. In this work, BHMF is enzymatically polymerized with various diacid ethyl esters by *Candida antarctica* lipase b (CALB) via a two-stage, three-step method. A series of novel biobased furan polyesters are successfully produced, with number average molecular weights ($\bar{M}_n$) of around 2000 g/mol. $^1$H-NMR and MALDI-ToF MS analysis indicate that etherification side reactions occur during the enzymatic polymerization, which lead to the formation of low molecular weight products. Moreover, the chemical structures, microstructures and end groups, and crystalline and thermal properties of the synthetic BHMF-based polyesters are extensively investigated. Furthermore, the effects of the number of the methylene units in the dicarboxylic segments on the physical properties of the obtained furan polyesters are discussed.

This chapter was published in: *Biomacromolecules* 2014, 15, (7), 2482-2493.
5.1 Introduction

Polyesters are widely used commodity polymers in our daily life. They are frequently applied in many areas such as in food containers, fibers, and packing and coating materials.\(^1\)\(^2\) Normally polyesters are synthesized from petroleum-based diacids and diols using metallic alkoxides as catalysts.\(^3\)\(^4\) As concerns on energy shortage and environmental pollution increase in recent years, seeking alternative biobased polyesters has attracted enormous attention both in academic and industrial fields.\(^5\)\(^7\) Benefiting from solar energy, various functional monomers produced from renewable biomass feedstocks are promising candidates for green polyester synthesis.\(^6\)\(^-\)\(^14\) These biobased monomers provide a great opportunity for achieving future sustainability.

*Candida antarctica* lipase b (CALB) is the most extensively studied enzyme in biocatalytic polyester synthesis.\(^2\)\(^4\)\(^15\)\(^-\)\(^27\) CALB shows broad substrate adaptability and stable catalytic performance in different chemical environments.\(^4\)\(^28\)\(^-\)\(^30\) Compared to many conventional catalysts, CALB is capable to produce novel polyesters containing sensitive structures without toxic residuals; therefore the products have found promising applications in biomedical and pharmaceutical fields.

Currently CALB-catalyzed synthesis of biobased polyesters from renewable resources has gained increasing popularity. Many biobased monomers have been studied,\(^31\)\(^-\)\(^41\) for example, succinate, fatty acids from vegetable oils, isohexides derived from sugars, 1,4-butanediol, glycerol, and so on.

2,5-Bis(hydroxymethyl)furan (BHMF) is a highly valuable green building block adequate for polyester synthesis.\(^42\) It can be converted easily from 5-hydroxymethylfurfural that is derived from various carbohydrates.\(^11\)\(^43\)\(^-\)\(^46\) This diol has a rigid furan structure, rendering polyesters with higher glass transition temperatures and better mechanical properties.\(^13\)\(^42\) Surprisingly, BHMF has not been well studied for polyester synthesis yet. Among the reported studies related to BHMF-based polyesters, Hatanak *et al*.\(^47\) investigated the polycondensation of BHMF with succinate, fumarate, or maleate derivatives without catalyst or using \(N,N'\)-dicyclohexylcarbodiimide as a condensing reagent; and recently, Yoshie *et al*.\(^48\)\(^,\)\(^49\) prepared biobased furan polymers with self-healing ability from succinic acid, 1,4-butanediol and BHMF by \(N,N'\)-diisopropylcarbodiimide; and Habeych N. studied the lipase-catalyzed polymerization with BHMF which only yielded a mixture of linear and cyclic furan oligomers.\(^50\) To the best of our knowledge, the
enzyme-catalyzed synthesis of BHMF-based polyesters with high molecular weights has not been studied up until now.

We present here a total eco-friendly synthesis approach towards furan polyesters. In this approach, BHMF and various diacid ethyl esters differing in chain length are enzymatically polymerized via a two-stage, three-step method in the presence of CALB; and BHMF-based polyesters with different structures are successfully prepared. Moreover, the molecular weights, chemical structures, microstructures and end groups, crystalline properties, and thermal properties of the synthesized BHMF-based polyesters are carefully investigated.

5.2 Experimental Methods

5.2.1 Materials

Lipase acrylic resin from Candida antarctica lipase b (CALB, in immobilized form as Novozym® 435, 5000+ U/g), diethyl succinate (99 %), diethyl glutarate (99+ %), diethyl adipate (99 %), diethyl sebinate (98+ %), chloroform (HPLC grade) and diphenyl ether (99 %) were purchased from Sigma-Aldrich. Diethyl dodecanedioate (95+ %) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99+ %) were purchased from TCI Europe. Diethyl suberate (99 %) was purchased from ABCR. 2,5-Bis(hydroxymethyl)furan (BHMF, 98+ %) was purchased from Apollo Scientific. Diphenyl ether was vacuum distilled and stored with 4 Å molecular sieves before use. The other chemicals were used as received.

5.2.2 General Procedure for CALB-Catalyzed Polycondensation of Diacid Ethyl Esters and BHMF in Diphenyl Ether via a Two-Stage, Three-Step Method

CALB (0.1 g) was fed into a 25 mL flask and stored in a desiccator with phosphorus pentoxide at room temperature under a high vacuum for 16 h. Then diacid ethyl ester (3.9 mmol), BHMF (3.9 mmol), and diphenyl ether (2 g) were added into the flask. We performed the enzymatic polymerization according to the following procedure as reported in literature:31 (1) maintaining the reaction at 80 ºC for 2 h under an atmospheric pressure with a tiny nitrogen flow, (2) regulating the reaction pressure to 350 mmHg while maintaining the reaction at 80 ºC for 4 h, (3) reducing the reaction pressure to 2 mmHg while maintaining the reaction at the same temperature for 66 h.
Chloroform (20 mL) was introduced to terminate the enzymatic polymerization. CALB was filtered off and washed with chloroform (20 mL) three times. The solutions were then combined and concentrated by rotary evaporation at 40 °C under a vacuum of 300 mmHg. Then the condensed solution was added dropwise into excess of cold methanol (-20 °C) for precipitation. After that, the methanol solution with the precipitates was stored still at -20 °C for 24 h. Then, the precipitates were collected by vacuum filtration and washed with methanol (15 mL) three times. Finally, the products were dried in a vacuum oven at room temperature for 2 - 3 days before analysis. The obtained BHMF-based polyesters were pale yellow semicrystalline powders.

**Poly(2,5-furandimethylene succinate) (PFMS)** \(^1^H\)-NMR (400 MHz, CDCl\(_3\)-d\(_1\), ppm): 6.35 (2H, s, -CH=, furan), 5.03 (4H, s, -CO-O-CH\(_2\)-), 2.65 (4H, m, -CO-O-CH\(_2\)-, succinate), 4.45 (s, -CH\(_2\)OH, end group from BHMF), 4.11 (m, -OCH\(_2\)CH\(_3\), end group from diethyl succinate), 1.22 (t, -OCH\(_2\)CH\(_3\), end group from diethyl succinate); \(^1^3^C\)-NMR (100 MHz, CDCl\(_3\)-d\(_1\), ppm): 171.71 (=C=, furan), 150.23 (=C(C)-O-, furan), 111.27 (=C-, furan), 58.44 (=O-CO-CH\(_2\)-), 63.47 (-CH\(_2\)OH, end group), 63.47 (-OCH\(_2\)CH\(_3\), end group), 13.81 (-OCH\(_2\)CH\(_3\), end group).

**Poly(2,5-furandimethylene glutarate) (PFMG)** \(^1^H\)-NMR (400 MHz, CDCl\(_3\)-d\(_1\), ppm): 6.35 (2H, s, -CH=, furan), 5.02 (4H, s, -CO-O-CH\(_2\)-), 2.39 (4H, m, -CO-O-CH\(_2\)-, glutarate), 1.96 (2H, m, -CH\(_2\)-, glutarate), 4.45 (s, -CH\(_2\)OH, end group from BHMF), 4.12 (m, -OCH\(_2\)CH\(_3\), end group from diethyl glutarate), 1.23 (t, -OCH\(_2\)CH\(_3\), end group from diethyl glutarate); \(^1^3^C\)-NMR (100 MHz, CDCl\(_3\)-d\(_1\), ppm): 172.46 (=C=, furan), 150.23 (=C(C)-O-, furan), 111.27 (=C-, furan), 58.24 (=O-CO-CH\(_2\)-), 33.26 (=O-CO-CH\(_2\)-), 19.87 (-CH\(_2\)-), 63.51 (-CH\(_2\)OH, end group), 60.23 (-OCH\(_2\)CH\(_3\), end group), 14.07 (-OCH\(_2\)CH\(_3\), end group).

**Poly(2,5-furandimethylene adipate) (PFMA)** \(^1^H\)-NMR (400 MHz, CDCl\(_3\)-d\(_1\), ppm): 6.35 (2H, s, -CH=, furan), 5.02 (4H, s, -CO-O-CH\(_2\)-), 2.34 (4H, m, -CO-O-CH\(_2\)-, adipate), 1.64 (4H, m, -CH\(_2\)-, adipate), 4.46 (s, -CH\(_2\)OH, end group from BHMF), 4.10 (m, -OCH\(_2\)CH\(_3\), end group from diethyl adipate), 1.23 (t, -OCH\(_2\)CH\(_3\), end group from diethyl adipate); \(^1^3^C\)-NMR (100 MHz, CDCl\(_3\)-d\(_1\), ppm): 172.67 (=C=, furan), 150.14 (=C(C)-O-, furan), 111.07 (=C-, furan), 58.03 (=O-CO-CH\(_2\)-), 34.05 (=O-CO-CH\(_2\)-), 24.44 (-CH\(_2\)-), 63.50 (-CH\(_2\)OH, end group), 60.30 (-OCH\(_2\)CH\(_3\), end group), 14.29 (-OCH\(_2\)CH\(_3\), end group).

**Poly(2,5-furandimethylene suberate) (PFMSu)** \(^1^H\)-NMR (400 MHz, CDCl\(_3\)-d\(_1\), ppm): 6.34 (2H, s, -CH=, furan), 5.01 (4H, s, -CO-O-CH\(_2\)-), 2.30 (4H, m, -O-CO-
CH$_2$-, suberate), 1.60 (4H, m, -CH$_2$-, suberate), 1.30 (4H, m, -CH$_2$-, suberate), 4.45 (s, -CH$_2$:OH, end group from BHMF), 4.09 (m, -OCH$_2$CH$_3$, end group from diethyl suberate), 1.23 (t, -OCH$_2$CH$_3$, end group from diethyl suberate); $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, ppm): 172.46 (=$C$-furan), 5.02 (4H, s, -CO-O-C), 6.35 (2H, s, -CH$_2$H$_2$-, suberate), 1.23 (t, -OCH$_2$CH$_3$, end group from diethyl suberate); $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, ppm): 57.86 (-CO-O-CH$_2$-), 33.95 (-O-CO-CH$_2$-), 28.97 (-CH$_2$-), 24.59 (-CH$_2$-), 63.70 (-CH$_2$OH, end group), 60.32 (-OCH$_2$CH$_3$, end group), 14.00 (-OCH$_2$CH$_3$, end group).

Poly(2,5-furandimethylene sebacate) (PFMSe) $^1$H-NMR (400 MHz, CDCl$_3$-$d_1$, ppm): 6.34 (2H, s, -CH=, furan), 5.02 (4H, s, -CO-O-CH$_2$-), 2.32 (4H, m, -O-CO-CH$_2$-, sebacate), 1.59 (4H, m, -CH$_2$-, sebacate), 1.26 (8H, m, -CH$_2$-, sebacate), 4.46 (s, -CH$_2$:OH, end group from BHMF), 4.11 (m, -OCH$_2$CH$_3$, end group from diethyl sebacate), 1.23 (m, -OCH$_2$CH$_3$, end group from diethyl sebacate); $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, ppm): 173.28 (=$C$=O), 150.23 (=C(C)-O-, furan), 111.26 (=$C$-, furan), 57.86 (-CO-O-CH$_3$-), 34.46 (-O-CO-CH$_2$-), 28.99 (-CH$_2$-), 24.63 (-CH$_2$-), 63.50 (-CH$_2$:OH, end group), 60.34 (-OCH$_2$CH$_3$, end group), 14.72 (-OCH$_2$CH$_3$, end group).

Poly(2,5-furandimethylene dodecanedioate) (PFMD) $^1$H-NMR (400 MHz, CDCl$_3$-$d_1$, ppm): 6.35 (2H, s, -CH=, furan), 5.02 (4H, s, -CO-O-CH$_2$-), 2.31 (4H, m, -O-CO-CH$_2$-, dodecanedioate), 1.58 (4H, m, -CH$_2$-, dodecanedioate), 1.24 (12H, m, -CH$_2$-, dodecanedioate), 4.46 (s, -CH$_2$:OH, end group from BHMF), 4.11 (m, -OCH$_2$CH$_3$, end group from diethyl dodecanedioate); $^{13}$C-NMR (100 MHz, CDCl$_3$-$d_1$, ppm): 173.14 (=$C$=O), 150.43 (=C(C)-O-, furan), 111.49 (=$C$-, furan), 57.61 (-CO-O-CH$_2$-), 34.25 (-O-CO-CH$_2$-), 29.17 (-CH$_2$-), 24.80 (-CH$_2$-), 59.97 (-OCH$_2$:CH$_3$, end group), 14.29 (-OCH$_2$:CH$_3$, end group).

### 5.2.3 Control Reactions

Diacid ethyl esters and BHMF were polymerized without CALB according to the same procedure as described in Section 5.2.2. After the reaction, no polyester was obtained in all the control reactions after precipitation in cold methanol (−20 °C). However, a small amount of yellow products adhered to the bottle surface after the reaction. They were insoluble in chloroform but dissolved in HFIP. Therefore, the reaction bottle was washed with HFIP three times. The combined solutions were concentrated and then added dropwise into cold methanol (−20 °C). After that, a tiny amount of dark yellow products were obtained by centrifugation. Subsequently, the remaining methanol solution was concentrated and then added dropwise into cold diethyl ether (5 °C). After that, a tiny amount of yellow products were obtained by centrifugation. The obtained products were dried in a...
vacuum oven at room temperature for 3 days. The dark yellow product precipitated in methanol was insoluble in DMSO-\(d_6\) and CDCl\(_3\)-\(d_1\), while the yellow product precipitated in diethyl ether was dissolved in DMSO-\(d_6\) for \(^1\)H-NMR analysis.

BHMF (3.9 mmol) and ethanol (7.8 mmol) were reacted with or without CALB in diphenyl ether via the two-stage, three-step method. At pre-selected time intervals, about 20 mg of the solution was withdrawn from the reaction. They were added directly into a NMR tube containing 1 g of DMSO-\(d_6\) for \(^1\)H-NMR analysis. After the reaction, HFIP was used to dissolve the yellow products that adhered to the bottle surface. The obtained solutions were then concentrated and precipitated in cold methanol (-20 °C). After that, the precipitates were collected by centrifugation. Finally, the obtained yellow products were dried in a vacuum oven at room temperature for 3 days before \(^1\)H-NMR analysis.

BHMF was mixed with or without CALB in diphenyl ether under the same polymerization conditions. After 24 h reaction, the insoluble yellow products were taken away from the bottle surface. They were dissolved in DMSO-\(d_6\) for \(^1\)H-NMR analysis.

5.2.4 \(^1\)H-NMR Investigation of CALB-Catalyzed Polycondensation of BHMF and Diacid Ethyl Esters in Diphenyl Ether via the Two-Stage, Three-Step Method

Diacid ethyl ester (3.9 mmol, diethyl succinate/diethyl suberate/diethyl dodecanedioate), BHMF (3.9 mmol), and diphenyl ether (2 g) were added into a flask with or without pre-dried CALB (0.1 g). The two-stage, three-step method was applied to all the reactions according to the same procedures as described in Section 5.2.2.

At pre-selected time intervals, about 20 mg of the solution was withdrawn from the reaction. They were added directly into a NMR tube containing 1 g of CDCl\(_3\)-\(d_1\) for \(^1\)H-NMR analysis.

5.2.5 Instrumental Methods

\(^1\)H- and \(^1\)H-NMR spectra were recorded on a Varian VXR spectrometer (400 MHz for \(^1\)H-NMR and 100 MHz for \(^1\)H-NMR analysis), using CDCl\(_3\)-\(d_1\) as the solvent. The chemical shifts reported were referenced to the resonances of tetramethylsilane (TMS) or the solvent. The number average molecular weight (\(\overline{M}_n\)) was calculated from \(^1\)H-NMR using the following equation, 

\[
\overline{M}_n = \left(\frac{L_E}{4} \times M_E + \frac{L_{DA}}{4} \times M_{DA}\right) / [0.5 \times
\]

\[\ldots\]
\[
\left(\frac{I_{E-F}}{2} + \frac{I_{E-D\alpha}}{2}\right) + M_E, \text{ where } I_F \text{ is the integral intensity of the singlet assigned to the BHMF methylene protons (-CO-O-CH_2-) at around 5.0 ppm, } I_{D\alpha} \text{ is the integral intensity of the broad peaks ascribed to the methylene protons (-O-CO-CH_2-) from the dicarboxylic segments at around 2.3 - 2.7 ppm, } I_{E-F} \text{ is the integral intensity of the singlet assigned to the BHMF methylene end groups at around 4.5 ppm, } I_{E-D\alpha} \text{ is the integral intensity of the broad peaks belonging to the ester end groups at around 4.1 ppm, } M_F \text{ is the molecular mass of the furanic repeating unit, } M_{D\alpha} \text{ is the molecular mass of the dicarboxylic repeating unit, } M_E \text{ is the molecular mass of the end groups. Here we assumed that all furan polyester was terminated with OH/ester groups.}
\]

Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) measurements were carried out on a Bruker IFS88 FT-IR spectrometer.

The molecular weights \((\bar{M}_n \text{ and } \bar{M}_w)\) and dispersity \((D, \bar{M}_w/\bar{M}_n)\) were measured by Size Exclusion Chromatography (SEC) at 30 °C using a Viscotek SEC equipped with a triple detector. Chloroform of HPLC grade was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calculations were performed based on the universal calibration. Narrow dispersity polystyrene standards (Agilent and Polymer Laboratories), with \(\bar{M}_w\) values ranging from 645 to 3001000 g/mol, were used to generate the universal calibration curve.

The glass transition temperature \((T_g)\) and melting temperature \((T_m)\) were measured by Differential Scanning Calorimetry (DSC) using a TA-Instruments Q1000 DSC. The heating and cooling rate were 10 °C/min.

Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer Thermo Gravimetric Analyzer TGA7. Samples were measured at the scan rate of 10 °C/min under a nitrogen environment.

Wide-angle X-ray diffraction (WAXD) was performed using a Bruker D8 Advance diffractometer in the angular range of 10 - 30° (2θ). The degree of crystallinity \((\chi_c)\) was calculated from WAXD\(^{32, 46}\) using the following equation, \(\chi_c \, \text{(\%)} = 100 \times k \times I_c/(I_c + I_a), \) where \(k\) is the relative scattering factor between the crystal part and the amorphous part of a polymer (normally \(k = 1\) since it is difficult to figure out), \(I_c\) are the integral intensities of the crystal peaks; \(I_a\) is the integral intensity of the amorphous halo. \(I_c\) and \(I_a\) values were determined with the Peak Analyzer-Fit Peaks (pro) tool of OriginPro 9.1 software (OriginLab Corporation).

Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-ToF MS) measurements were performed on a Biosystems Voyager-DE
PRO spectrometer. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB). First, DCTB (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 - 2 mg/mL) in HFIP were premixed in a ratio of 5:1:5. The mixture was then subsequently hand-spotted on a stainless steel plate and left to dry. After that, the mass spectra were recorded in positive and linear mode.

5.3 Results and Discussion

BHMF and diacid ethyl esters were polycondensed in the presence of CALB; and a series of novel biobased furan polyesters with different chemical structures were produced (Scheme 5.1). The diacid ethyl esters used included (potentially) biobased diethyl succinate, diethyl glutarate, diethyl adipate, diethyl suberate, diethyl sebacate, and diethyl dodecanedioate. The number of the methylene units \( n \) in the dicarboxylic segments is 2, 3, 4, 6, 8, and 10 respectively.

![Scheme 5.1](image.png)

**Scheme 5.1.** The CALB-catalyzed synthesis of BHMF-based polyesters using the two-stage, three-step method.

5.3.1 CALB-Catalyzed Polycondensation of BHMF with Various Diacid Ethyl Esters in Diphenyl Ether

A two-stage, three-step method\(^{31, 41, 51, 52}\) was applied for the enzymatic synthesis of BHMF-based polyesters. At the first stage, BHMF and diacid ethyl esters were oligomerized by CALB under an atmospheric pressure during the first step and then under a low vacuum during the second step. At the second stage (the third step), oligomers were further polycondensed to produce polyesters under a high vacuum. During the enzymatic polymerization, we observed that continuous bubbles emerged from the reaction media immediately after applying a high vacuum; and alcohol byproducts were gradually congealed in the cold trap. These suggested the occurrence of polyesterification with generation of alcohols.

The chemical structures of the obtained BHMF-based polyesters were confirmed by \(^1\)H- and \(^{13}\)C-NMR spectra (see Figure 5.1). Here the NMR spectra of PFMS are discussed as an example. The single peak at around 6.35 ppm was ascribed to the furanic protons and the other peak at around 5.03 ppm was assigned to the...
methylene protons linked to the furan rings, due to the symmetry of BHMF; and these two characteristic peaks appeared in the $^1$H-NMR spectra of all the tested BHMF-based polyesters (Figure 5.1a). In addition, the broad peak at 2.65 ppm was assigned to the residue methylene protons from succinate, and the low intensity resonances at 4.45, 4.11 and 1.22 ppm were the proton signals from the end groups. Furthermore, in the $^{13}$C-NMR spectrum of PFMS (see Figure 5.1b), the characteristic peaks at 150.23, 111.27 and 58.44 ppm were ascribed to the carbons from BHMF; the peak at 171.71 ppm was assigned to the carbon from the newly formed carboxyl groups; the resonance at 28.09 ppm belonged to the methylene carbons from succinate; and the low intensity peaks at 63.67, 63.47 and 13.81 were carbon signals from the end groups.

**Figure 5.1.** (a) $^1$H-; and (b) $^{13}$C-NMR spectra of the obtained BHMF-based polyesters.

The chemical structures of the synthetic BHMF-based polyesters were further characterized by ATR-FTIR spectroscopy, as plotted in Figure 5.2. The following characteristic bands were assigned to the furan ring, including the C-H stretching vibrations at 3135 cm$^{-1}$, the C=C ring stretching vibrations at 1560 cm$^{-1}$, the ring vibrations of the =C-O-C= groups at 980 - 1045 and 1150 cm$^{-1}$, as well as, the out-of-plane deformation vibrations of the C-H groups at 900 - 976, 760 - 840, and 700 - 760 cm$^{-1}$. In addition, the two bands at 2910 - 2960 and 2864 - 2848 cm$^{-1}$ were ascribed to the asymmetric and symmetric stretching vibrations of the CH$_2$ groups respectively; the strong band at 1730 cm$^{-1}$ was due to the C=O stretching vibrations; and the multi-bands at 1435 - 1470 and 1385 - 1420 cm$^{-1}$ were ascribed to the deformation and wagging vibrations of the CH$_2$ groups respectively. Moreover, the bands at 1200 - 1260 and 1150 cm$^{-1}$ were assigned to the
asymmetric and symmetric stretching vibrations of the ester C-O-C groups, respectively.

Figure 5.2. ATR-FTIR spectra of the tested BHMF-based polyesters.

Table 5.1. Result summary: CALB-catalyzed polycondensation of BHMF with various diacid ethyl esters in diphenyl ether, using the two-stage, three-step method

<table>
<thead>
<tr>
<th>Polyester</th>
<th>( n )</th>
<th>NMR (^a)</th>
<th>SEC (^c)</th>
<th>MALD-ToF MS (^d)</th>
<th>Yield (^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( M_n )</td>
<td>( M_{av} )</td>
<td>( M_w )</td>
<td>( D )</td>
</tr>
<tr>
<td>PFMS</td>
<td>2</td>
<td>1500</td>
<td>2100</td>
<td>2700</td>
<td>1.29</td>
</tr>
<tr>
<td>PFMG</td>
<td>3</td>
<td>1900</td>
<td>2100</td>
<td>3600</td>
<td>1.71</td>
</tr>
<tr>
<td>PFMA</td>
<td>4</td>
<td>2400</td>
<td>2200</td>
<td>3400</td>
<td>1.55</td>
</tr>
<tr>
<td>PFMSu</td>
<td>6</td>
<td>1800</td>
<td>2400</td>
<td>3300</td>
<td>1.38</td>
</tr>
<tr>
<td>PFMSe</td>
<td>8</td>
<td>1900</td>
<td>2200</td>
<td>3600</td>
<td>1.64</td>
</tr>
<tr>
<td>PFMD</td>
<td>10</td>
<td>1900</td>
<td>2200</td>
<td>3900</td>
<td>1.77</td>
</tr>
</tbody>
</table>

\(^a\) The number of the methylene units in the dicarboxylic segments; \(^b\) Calculated from \(^1\)H-NMR; \(^c\) Determined by SEC in chloroform using the universal calibration method; \( M_n \) = the number average molecular weight (g/mol), \( M_{av} \) = the weight average molecular weight (g/mol), \( D = M_w / M_n \) (dispersity); \(^d\) \( M_n = \sum I_i M_i \sum I_i \); \( M_w = \sum I_i M_i^2 \sum I_i \); \( I_i \) is the integration intensity of the mass peak \( i \) from the MALDI-ToF MS spectra; \( M_i \) is the molecular mass of the peak \( i \); \(^e\) Isolated yield (%) after precipitation in cold methanol.

The molecular weights of the synthesized BHMF-based polyesters were determined by SEC. All the obtained polyesters possessed a similar retention volume ranging from 14.5 to 18.5 mL. This suggested that the enzymatic polycondensation yielded low molecular weight products. As listed in Table 5.1, the \( M_n \) values of all the obtained BHMF-based polyesters were low and similar, around 2100 - 2400 g/mol. However, the dispersity (\( D \)) was quite good, around 1.29 - 1.77. This was due to the fact that the conversion of the diacid ethyl esters
and the OH groups of BHMF was very low. Moreover, the reaction yield is a bit low, between 60 – 74 %.

We also calculated the molecular weights from $^1$H-NMR and MALDI-ToF MS, which gave $\bar{M}_n$ values of around 1500 - 2400 g/mol and 1600 - 2400 g/mol, respectively. These values are quite in consistence with the SEC results.

The CALB-catalyzed polycondensation was studied by $^1$H-NMR (Figure 5.3a). BHMF was enzymatically polymerized with three diacid ethyl esters, including diethyl succinate ($n = 2$), diethyl suberate ($n = 6$), and diethyl dodecanedioate ($n = 10$); and the corresponding product $\bar{M}_n$ at different polymerization time was determined by $^1$H-NMR, as presented in Figure 5.4.

![Figure 5.3](image)

**Figure 5.3.** (a) $^1$H-NMR spectra of the solution mixtures from the CALB-catalyzed polycondensation of BHMF and diethyl succinate via the two-stage, three-step method; and (b) $^1$H-NMR spectra of the solution mixtures from the control reaction of BHMF and diethyl succinate in the absence of CALB via the two-stage, three-step method. The spectra were recorded in CDCl$_3$-d$_1$ and normalized by the peak at around 5.0 ppm.

BHMF-based oligomers were produced in the reaction at 80 °C for 0.25 h as proven by $^1$H-NMR, including the appearance of the new peak assigned to the methylene protons of BHMF at around 5.0 ppm, the shift of the furanic proton signals from 6.2 to 6.3 ppm, and the presence of the methylene proton peaks from the ethanol byproduct at around 3.7 ppm. The product $\bar{M}_n$ calculated from $^1$H-NMR was around 200 - 300 g/mol, which suggested that only dimers were produced. As the polymerization time was increased from 0.25 to 2 h at the first step under an atmospheric pressure, the ethanol byproduct and the OH groups of
BHMF were still observed. Meanwhile, the intensity of the ester end group signals at around 4.1 ppm decreased slightly, while the intensity of the furanic proton resonances at 6.3 ppm increased. However, the product $M_n$ remained almost unchanged (around 200 - 300 g/mol), suggesting that more dimers were produced. In addition, the peak intensity of the furanic proton resonance assigned to BHMF at around 6.2 ppm remained almost the same. This clearly showed that the concentration of BHMF in the reaction mixture was constant at the first step since BHMF has a low solubility in the tested media.

As the polymerization time was extended from 2 to 6 h under a low vacuum of 350 mmHg, the intensity of the following peaks obviously decreased, including the furanic proton signals assigned to BHMF, the methylene proton resonances from the ethanol byproduct, and the peaks ascribed to the ester end groups. This suggested that more monomers were converted to oligomers by CALB. Meanwhile, the product $M_n$ increased slightly, similar to that of the dimers and trimers. This indicated that the low vacuum applied at the second step did not help much for the chain growth of BHMF oligomers but facilitated the monomer conversion.

After applying the high vacuum (2 mmHg) at the third step, the peaks assigned to the ethanol byproduct disappeared, indicating that all the ethanol generated during the polycondensation was eliminated from the reaction. Moreover, the furanic proton resonances at around 6.2 ppm disappeared completely after 22 h reaction, which suggested that all BHMF was converted to oligoesters or polyesters. As presented in Figure 5.4, the product $M_n$ increased significantly from around 300 to

**Figure 5.4.** Plot of the number average molecular weight ($M_n$) against the polymerization time. The $M_n$ values were calculated from the $^1$H-NMR spectra of the solution mixtures withdrawn from the CALB-catalyzed polycondensation of BHMF and diacid ethyl esters.
1200 - 1400 g/mol with increasing the reaction time from 6 h to 31 h. After that, it reached a plateau value at around 1300 - 1500 g/mol.

We also investigated the control reactions of BHMF and diacid ethyl esters (diethyl succinate, diethyl suberate and diethyl dodecanedioate) without CALB. As the representative $^1$H-NMR spectra shown in Figure 5.3b, no resonance can be assigned to the BHMF-based oligoesters or polyesters. This confirmed that the polyesterification was indeed catalyzed by the enzyme CALB.

It is surprising that diacid ethyl esters with different chain length had no significant influence on the molecular weights of BHMF-based polyesters synthesized from the CALB-catalyzed polymerization. This was not in accordance with previous results reported in literature.$^2, 36, 54$ It was found that the enzymatic polymerization of aliphatic diols and α,ω-linear aliphatic diacids with six or more carbons usually yielded polyesters with much higher molecular weights. In this work, the independence between the enzymatic polymerization and diacid ethyl esters with different chain length was due to the formation of ethers. This is because the OH groups of BHMF are very reactive. They can dehydrate together to form BHMF ethers on one hand and react with the ethanol byproduct to produce ether end groups on the other hand. This was confirmed by the $^1$H-NMR study (see Figure 5.3b) and the MALDI-ToF MS analysis (see Section 5.3.2), respectively.

As shown in Figure 5.3b, the formation of BHMF ethers by the self-dehydration between the OH groups of BHMF was proven by the appearance of a small resonance at around 4.40 ppm, and BHMF ethers were already produced after 0.25 h reaction. This is due to the fact that BHMF has a low solubility in the tested media. It melted at around 74 - 77 °C but cannot disperse in the tested media during the temperature rise period at the beginning. Therefore, the active OH groups of BHMF dehydrated to form BHMF ethers which are insoluble in the tested media and adhered to the flask surface. This agreed well with our observation that a tiny amount of yellow products stuck to the bottle surface after the enzymatic polymerization. Furthermore, the BHMF ethers were identified in the isolated yellow products, as confirmed by $^1$H-NMR.

The BHMF-based oligoesters and polyesters are soluble in the tested media. In this case the etherification between the OH groups of BHMF was suppressed during the enzymatic polymerization since the CALB-catalyzed polyesterification is much faster. This explained well why the peak intensity of the ether resonance was rather low and did not increase with increasing polymerization time (see Figure 5.3a). Besides this, in the control reactions without CALB, more BHMF ethers were
formed by the dehydration between the OH groups of BHMF. As shown in Figure 5.3b, the peak intensity of the resonances assigned to protons in BHMF ethers increased significantly with polymerization time at the third step. Moreover, the yellow sticky products from the control reactions were purified by precipitation in methanol and in diethyl ether. Their $^1$H-NMR spectra clearly proven that BHMF ethers were produced from the control reaction without CALB.

To further confirm the etherification between the OH groups of BHMF, BHMF was reacted with itself in diphenyl ether using the same two-stage, three-step method. As proven by the $^1$H-NMR, such etherification occurred in both reactions with or without CALB. We also found that the etherification between the OH groups of BHMF was inhibited in the presence of CALB since less BHMF ethers were produced in the control reaction with CALB. This is reasonable because BHMF could enter into the active site of CALB and, therefore, the OH groups of BHMF were protected.

As suggested by MALDI-ToF MS analysis (see 5.3.2), ether end groups could be produced by the reaction between OH groups of BHMF and ethanol byproduct. To verify this, BHMF and ethanol were reacted in diphenyl ether with or without CALB via the same two-stage, three-step method. It seemed that only a tiny amount of the OH groups of BHMF reacted with ethanol in the presence of CALB and this probably occurred during the first and the second step. This was further confirmed by the $^1$H-NMR study since the resonances assigned to the ether end groups that were formed by reaction between ethanol and OH groups of BHMF were not identified (see Figure 5.3b). Moreover, the etherification between ethanol and the OH groups of BHMF did not occur in the control reaction without CALB.

In conclusion, etherification side reactions occurred during the enzymatic polymerization in this study. As a consequence, BHMF ethers were formed by the dehydration between the OH groups of BHMF, and ether end groups were produced by the reaction between the OH groups of BHMF and ethanol byproduct. These explained well why the enzymatic polymerization did not change with diacid ethyl esters having different chain length. On the one hand, the etherification side reaction changed the stoichiometric ratio between the OH groups and ethyl ester groups. One the other hand, the ether end groups hindered the chain growth of polyesters at one end. Therefore, only low molecular weight BHMF-based polyesters were produced in this study. However, the occurrence of etherification side reactions during the enzymatic polymerization could be prevented in the future by reducing the reaction temperature, shortening the reaction time at the first and second step, or using other solvents which are miscible with BHMF.
5.3.2 MALDI-ToF MS Analysis of the Obtained BHMF-Based Polyesters: Microstructures with Different End Groups

Figure 5.5a depicts the overlay MALDI-ToF MS spectra of the obtained furan polyesters. We observed similar mass peak patterns for all the tested polyesters in a m/z region of 500 - 6000 g/mol.

The microstructures of the obtained BHMF-based polyesters were determined by equation 5.1:

\[ M = M_{\text{end group}} + (n \times M_{\text{repeating unit}}) + M_{K^+} \]  \hspace{1cm} (Equation 5.1)

where \( M \) is the molecular mass of a polymer, \( M_{\text{end group}} \) is the molecular mass of the end group; \( n \) is the number of the repeating unit, \( M_{\text{repeating unit}} \) is the molecular mass of the repeating unit, and \( M_{K^+} \) is the molecular mass of potassium.

![Figure 5.5a: Overlay MALDI-ToF MS spectra of BHMF-based polyesters.](image)

![Figure 5.5b: Representative mass spectrum of poly(2,5-furandimethylene succinate) (PFMS) with peak interpretations.](image)

Four microstructures are present in all the tested BHMF-based polyesters, as listed in Table 5.2. They are terminated with ester/ester, ether/ester, and hydroxyl/ester end groups, respectively, as well as, cyclic without end groups. Figure 5.5b illustrates the representative mass spectrum of PFMS with peak interpretations. The dominant peak series represented furan polyesters terminated with ester/ester groups. The other significant peak series with the intensity of around 8 % were assigned to furan polyesters with ether/ester end groups. A possible explanation for this observation is that the ether end groups were produced by the highly reactive hydroxyl groups of BHMF with the ethanol byproduct generated from the
enzymatic polycondensation. In addition, cyclic furan polyesters and furan polyesters having hydroxyl/ester end groups were also identified. The peak series attributed to them showed a rather low intensity, below 5 %.

From the peak intensities we can conclude that the most abundant furan polyesters were terminated with ester/ester groups; small amount of the obtained polyesters had ether/ester end groups; and only trace amount of furan polyesters were cyclic or ended with hydroxyl/ester groups. However, this conclusion shall be taken with care since MALDI is not a quantitative technique. It is known that polymer chains could be more or less easily ionized depending on the chain-ends and low molar mass polymer chains are generally overestimated compared to its higher molecular weight counterparts.

**Table 5.2.** Microstructures and end groups of the tested BHMF-based polyesters

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Structure/Microstructure</th>
<th>Mass of the repeating units and end groups (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeating unit</td>
<td></td>
<td><img src="image" alt="Repeating unit" /></td>
<td>PFMS</td>
</tr>
<tr>
<td>Ester/Ester</td>
<td><img src="image" alt="Ester/Ester" /></td>
<td>174.2</td>
<td>188.2</td>
</tr>
<tr>
<td>Ether/Ester</td>
<td><img src="image" alt="Ether/Ester" /></td>
<td>74.1</td>
<td></td>
</tr>
<tr>
<td>-OH/Ester</td>
<td><img src="image" alt="OH/Ester" /></td>
<td>46.1</td>
<td></td>
</tr>
<tr>
<td>Cyclic</td>
<td><img src="image" alt="Cyclic" /></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Furthermore, no peak series could be assigned to the BHMF ethers that were produced by the dehydration between the OH groups of BHMF or polyesters with such BHMF ether groups. It is possible that all BHMF ethers were filtered off during the purification steps since they are not dissolved in chloroform. Moreover, the absence of mass peaks assigned to the polyesters having such BHMF ether groups in the MALDI-ToF MS spectra could be probably due to the fact that they had a rather low concentration in the final products.

**5.3.3 Crystalline Properties of the Obtained BHMF-Based Polyesters**

The obtained BHMF-based polyesters are pale yellow semicrystalline powders. Among them, PFMA, PFMSu, PFMSe and PFMD displayed similar WAXD patterns which exhibited six reflection peaks at 2θ of around 13.5 - 13.7 °, 17.3 - 17.4 °, 20.1 - 20.6 °, 21.5 - 21.7 °, 22.7 - 22.9 °, and 23.4 ° - 23.8 °, as shown in Figure 5.6a. This suggested that they possessed the same crystal structures.
Moreover, PFMS showed similar six diffraction peaks at these positions and it also had two extra reflection peaks at 18.8 and 19.9 °. This indicated that different crystal structures were formed in PFMS.

Moreover, PFMG showed reflection peaks at 16.6, 17.6, 19.9, 21.3, 23.4, and 24.5 °. Among these peaks, the two peaks at 16.6 and 17.6 ° are close to the reflection peaks at around 17.3 - 17.4 ° in the WAXD spectra of the other tested furan polyesters but they split up into two peaks; and the diffraction peaks at 19.9, 21.3, 23.4, and 24.5 ° are quite close to those reflection peaks at around 20.1 - 20.6 °, 21.5 - 21.7°, 22.7 - 22.9°, and 23.4 - 23.8° in the WAXD spectra of the other tested furan polyesters, but they are quite broad and shift a bit. Moreover, the small diffraction signal at 13.5 - 13.7 ° disappeared in the WAXD spectrum of PFMG. In conclusion, it is possible that the WAXD pattern of the tested PFMG was close to that of PFMA, PFMSu, PFMSe and PFMD but the crystallite size of the tested PFMG could be much smaller than the other tested furan polyesters; or it is possible that the tested PFMG possessed different crystal structures.

The representative multi-peak fitting of the WAXD spectrum is shown in Figure 5.6b; and a plot of the degree of crystallinity \( (\chi_c) \) and the enthalpy \( (\Delta H_m) \) of the obtained BHMF-based polyesters against the number of the methylene units in the dicarboxylic segments is shown in Figure 5.7. In general, the degree of crystallinity showed the same trend as the \( \Delta H_m \) values. They both increased with increasing amount of methylene units in the dicarboxylic segments. As shown in Figure 5.7, by changing the number of the methylene units from 2 to 10, the degree of crystallinity increased from 34 to 65 %, while the enthalpy value determined from
the first DSC heating curve increased from 37 to 85 J/g. This is because that the accumulation of methylene units enhanced the chain flexibility and facilitated chain packing, and therefore furan polyesters with longer methylene chains in the dicarboxylic moieties give rise to higher crystallinities. In addition, we noticed that the tested PFMG possessed a higher degree of crystallinity than the obtained PFMS and PFMA. This could be attributed to the peak simulation error caused by the broad diffraction signals. Actually the highest crystal peak of the tested PFMG at 21 ° from the peak simulations is quite broad. It is possible that this artificial crystal peak still contains some amorphous scattering signals. Therefore, the degree of crystallinity of the tested PFMG determined by WAXD would be higher than its real value. Besides, as we discussed before, the crystal structures of the tested PFMG could be different. This could also lead to a higher degree of crystallinity.

**Figure 5.7.** The degree of crystallinity ($\chi_c$) and enthalpy ($\Delta H_m$) as a function of the number of the methylene units in the dicarboxylic segments. The $\chi_c$ values were calculated from WAXD and the $\Delta H_m$ values were determined from the first DSC heating curves.

5.3.4 Thermal Properties of the Obtained BHMF-Based Polyesters

The thermal stability of the synthesized BHMF-based polyesters was determined by TGA. Figure 5.8 shows the TGA traces of BHMF-based polyesters. As presented in Table 5.3, the temperature at 5 % weight loss of all the tested polyesters ($T_{5\%}$) was around 253 - 300 °C, and two decomposition steps were observed in the TGA curves, with the temperatures of maximal rate of decomposition ($T_{d-max1}$ and $T_{d-max2}$) ranging from 276 - 332 °C and 436 - 453 °C, respectively. We also found that the weight losses were about 75 – 80 % and 11 – 16 % of the initial weight during the each step. Moreover, there was still around 8 – 11 % of the initial weights remained at 850 °C.
We also noticed that the $T_{5\%}$ and $T_{d-max1}$ of the tested polyesters increased with increasing number of methylene units in the dicarboxylic segments, which means the tested furan polyesters with longer methylene chains are more thermal stable. This is due to the fact that there are fewer amounts of C-O groups in the furan polyesters having similar molecular weights.

Figure 5.8. TGA traces of the tested BHMF-based polyesters: (a) weight (%) as a function of temperature (°C); and (b) derivative weight (%/°C) versus temperature (°C).

Table 5.3. Thermal and crystalline properties of the tested BHMF-based polyesters

<table>
<thead>
<tr>
<th>Polyester</th>
<th>TGA$^a$</th>
<th>DSC$^b$</th>
<th>WAXD$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{5%}$ ($^\circ$C)</td>
<td>$T_{d-max}$ ($^\circ$C)</td>
<td>$T_g$ ($^\circ$C)</td>
</tr>
<tr>
<td>PFMS</td>
<td>253</td>
<td>276/443</td>
<td>10</td>
</tr>
<tr>
<td>PFMG</td>
<td>290</td>
<td>290/436</td>
<td>-18</td>
</tr>
<tr>
<td>PFMA</td>
<td>270</td>
<td>300/446</td>
<td>-14</td>
</tr>
<tr>
<td>PFMSu</td>
<td>285</td>
<td>319/453</td>
<td>-27</td>
</tr>
<tr>
<td>PFMSu</td>
<td>292</td>
<td>327/452</td>
<td>-32</td>
</tr>
<tr>
<td>PFMD</td>
<td>300</td>
<td>332/452</td>
<td>-23</td>
</tr>
</tbody>
</table>

$^a$ $T_{5\%}$ ($^\circ$C) = the temperature of 5 % mass loss; $T_{d-max}$ ($^\circ$C) = the temperature of maximal rate of decomposition; $^b$ $T_g$ ($^\circ$C) = the glass transition temperature; $T_m$ ($^\circ$C) = the melting temperature; $\Delta H$ (J/g) = the enthalpy of transition; $T_c$ ($^\circ$C) = the crystallization temperature; $T_x$ ($^\circ$C) = the cold crystallization temperature upon heating; $\times$ = not detected; $^c$ $\chi_c$ (%) = the degree of crystallinity determined by WAXD; $^d$ Multiple melting temperatures observed; $^e$ Multiple cold crystallization temperatures and the corresponding enthalpy upon heating.

The thermal transitions of the obtained BHMF-based polyesters were investigated by DSC, as plotted in Figure 5.9 and Figure 5.10. For all the tested polyesters, broad and multiple melting peaks appeared in the first heating curves, with the $T_m$ values ranging from 43 - 86 °C. Figure 5.11a shows the plot of $T_m$ as a function of
the number of the methylene units in the dicarboxylic segments. Generally speaking, the \( T_m \) increases linearly as the methylene number varied from 3 to 10. This could be explained by the better packing capability of the polymer chains. We also noticed that the \( T_m \) of the tested PFMS observed from the first heating was surprisingly higher, which is close to that of the tested PFMD. This could be attributed to the different crystal structure of the tested PFMS and the relatively higher rigidity of 2,5-furandimethylene succinate units which is the shortest among the tested repeating units. Besides, the \( T_g \) of the tested PFMS is also relatively high, which also points to the relatively high chain rigidity.

**Figure 5.9.** DSC curves of the tested BHMF-based polyesters measured from -80 °C to 100 °C at the heating rate of 10 °C/min: (a) first heating curves; and (b) second heating curves.

Melting peaks disappeared in the second heating scans of the tested PFMS, PFMG and PFMA, while they were still observed in that of the tested PFMSu, PFMSe and PFMD. For the tested PFMS, PFMG and PFMA, no melting peak in the second heating is due to the fact that they crystallize very slowly. However, melting peaks appeared again in the second heating curve of the tested PFMS and PFMA if they stayed at 20 - 35 °C for extra 70 h during the cooling step. As for the tested PFMSu, PFMSe and PFMD, the \( T_m \) observed from the second heating curves was almost the same as that from the first heating curves. Meanwhile, we noticed that the corresponding \( \Delta H_m \) alters in the same trend as the \( T_m \) values when the number of the methylene units in the dicarboxylic segments increases from 3 to 10, as shown in Figure 5.11. This is in good agreement with the previous results as reported for isohexide-based polyesters.\(^{55}\) In other words, our results revealed that the crystallization rate and degree of crystallinity of the tested BHMF-based polyester are boosted by the enhancement of the number of methylene units in the polyester main chain.
Cold crystallization upon heating only occurred in the second heating of PFMSu (Figure 5.9b); and the crystallization peaks only appeared in the cooling curves of PFMSe and PFMD with longer methylene chains in the dicarboxylic moieties (Figure 5.10). The corresponding crystallization temperatures \( T_c \) were 28 and 46 °C, respectively. This further confirmed that the synthesized BHMF-based polyesters containing longer methylene chains crystallize faster.

![Figure 5.10. DSC cooling curves of the obtained BHMF-based polyesters.](image)

**Figure 5.10.** DSC cooling curves of the obtained BHMF-based polyesters.

![Figure 5.11.](image)

**Figure 5.11.** (a) Melting temperatures \( T_m \), maximum value) of the tested BHMF-based polyesters versus the number of the methylene units in the dicarboxylic segments, and (b) \( \Delta H_m \) of the tested BHMF-based polyesters as a function of the number of the methylene units in the dicarboxylic segments.

The glass transition temperatures \( T_g \) of the obtained BHMF-based polyesters are presented in Figure 5.9 and Table 5.3. As plotted in Figure 5.12, the \( T_g \) measured after eliminating thermal histories drops firstly from 4 to -38 °C as the number of the methylene units in the dicarboxylic segments varies from 2 to 6. This could be explained by the increasing of chain flexibility and mobility provided by the longer
methylene chains incorporated into the furan polyester chain. By further varying the methylene number from 6 to 10, the \( T_g \) however increased from -38 to -8 °C, which was due to the higher degree of crystallinity. This is due to the fact that the \( T_g \) of the semicrystalline polymers is often increased in temperature by the restricting of the molecular-motion through the crystallites.\(^{56}\)

**Figure 5.12.** Plot of glass transition temperatures (\( T_g \), second heating) of the tested BHMF-based polyesters against the number of the methylene units in the dicarboxylic segments.

Furthermore, we found that the \( T_g \) of the tested BHMF-based polyesters increased more than 24 °C compared to that of the aliphatic polyesters with a higher \( M_n \) synthesized from the same diacid ethyl ester with 1,4-butandiol. It is well known that the \( T_g \) is highly dependent on the \( M_n \), especially for polymers with low molecular weights. According to the Flory-Fox equation, the \( T_g \) increases with increasing the \( M_n \). Therefore the \( T_g \) of the low molecular weight aliphatic polyesters shall be much lower if their \( M_n \) is similar to the tested furan polyesters. In other words, the increase in \( T_g \) shall be much higher if the tested furan polyesters are compared to their low molecular weight aliphatic counterparts. Therefore, the huge rise in the \( T_g \) is due to the highly rigid furan rings in the polyester chains.

### 5.4 Conclusions

We have successfully synthesized and characterized novel BHMF-based polyesters by the CALB-catalyzed solution polycondensation of BHMF with various diacid ethyl esters. These biobased furan polyesters can have diverse applications in many areas such as in self-healing materials, biomedical materials, degradable materials and functional materials.
We found that etherification side reaction occur during the enzymatic polymerization; hence only low $\overline{M}_n$ products of around 2000 g/mol are obtained. To synthesize high molecular weight BHMF-based polyesters via enzymatic polymerization, the occurrence of etherification side reactions should be prevented, for example, by reducing the reaction temperature, shortening the reaction time at the first and second step, or using other suitable solvent.

The tested BHMF-based polyesters are semicrystalline. The degree of crystallinity ranges from 34 to 65 %, and the $T_m$ is around 43 - 86 °C. In addition, the tested furan polyesters are thermally stable up to 250 °C, showing two decomposition steps; and the $T_{d,max}$ at the major degradation step is around 276 - 332 °C. Moreover, the $T_g$ of the obtained BHMF-based polyesters are around -38 - 4 °C, which is significantly higher than that of the aliphatic counterparts.

The amount of methylene units in the dicarboxylic segments has significant influence on the crystalline and thermal properties of the tested BHMF-based polyesters. The degree of crystallinity, crystallization rate, $T_m$, $\Delta H_m$, and thermal stability are enhanced by increasing amount of methylene units incorporated into the polyester chains. Besides, the $T_g$ of the obtained polyesters decreases first as the amount of the methylene units in the dicarboxylic segments varies from 2 to 6. Then, the $T_g$ however, increases again as the methylene units in the dicarboxylic segments further changes from 6 to 10.

5.5 References


