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Environmentally benign synthesis of saturated and unsaturated aliphatic polyesters via enzymatic polymerization of biobased monomers derived from renewable resources

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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 $\overline{M_w}$ (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 relationships 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.

Introduction

Driven by the increasing demand to reduce greenhouse gas emission, to lower energy consumption, and to develop novel materials, biobased materials derived from yearly-based biomass feedstocks have attracted much attention both in academia and industry fields.[1-6] Among the biobased materials that may be considered, biobased aliphatic polyesters possess many appealing attributes. One of the most important attributes is that they are biodegradable materials which have a low environmental impact upon disposal.[7] Biobased aliphatic polyesters have broad potential applications in many fields such as fibers, packing materials, agricultural implements, tissue engineering scaffolds and drug delivery systems.[8-10]

In fact, most of aliphatic polyesters are renewable materials, as the majority of the synthetic building blocks can be derived from various carbohydrate sources, e.g., succinic acid, itaconic acid, 1,3-propanediol, 1,4-butanediol, 3-hydroxypropionic acid, α-methylene-γ-butyrolactone, etc.[1] One common pathway to synthetic aliphatic polyesters is by step-growth polymerization, in which aliphatic dicarboxylic acid derivatives and diols are polycondensed by an organometallic catalyst at elevated temperatures above 150 °C.[8] This approach is straightforward but suffers from two major drawbacks: (1) undesirable side-reactions may occur at high temperatures; and (2) removal of metal residues may be difficult. However, these problems can be readily circumvented by replacing the metal catalysts with biocatalysts: lipases.[11-16] Lipases are non-toxic enzymes derived from renewable resources. They catalyze the hydrolysis of lipids in living systems, and can also be used reversibly to catalyze the ester synthesis in water and some organic solvents.[14] Lipases have already been proven to be versatile in polyester synthesis at mild conditions.[11, 12, 14, 17, 18]

In addition, the side-reactions can be greatly suppressed in the lipase-catalyzed polymerization, and no harmful residues remain in the final products.

Among lipases, *Candida antarctica* Lipase B (CALB, in immobilized form as Novozym 435) is the working horse in biocatalytic polyester synthesis, as it possesses several crucial advantages such as broad substrate specificity, stable performance, and commercial availability.[14, 18-22]

The lipase-catalyzed synthesis of biobased polyesters is even more appealing since both monomer and enzyme catalyst are derived from renewable resources. This is an eco-friendly approach towards renewable polymeric materials.[5] By using this approach, the energy and material consumption can be greatly reduced and the generation of hazardous waste and

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† Electronic Supplementary Information (ESI) available: [^{13}C-NMR spectra, ATR-FTIR spectra; molar compositions, molecular weights, WAXD spectra, thermal properties, crystalline properties, and TGA traces of the obtained saturated and unsaturated aliphatic polyesters, the representative UV-cured unsaturated aliphatic polyester films and the representative ATR-FTIR spectrum of the UV cross-linked unsaturated aliphatic polyesters]. See DOI: 10.1039/x0xx00000x

emission can be remarkable minimized, which will benefit greatly to future sustainability.

Currently, many biobased polyesters have already been synthesized via lipase-catalyzed step-growth polymerization under mild conditions. For example, Gross *et al.* produced high molecular weight poly(butylene succinate) (PBS) via a temperature-varied two-stage method using CALB as catalyst.[23] Catalani *et al.* prepared a series of 1,4:3,6-dianhydrohexitol-based polyesters by CALB-catalyzed azeotropic polymerization.[24, 25] Kobayashi *et al.* enzymatically synthesized biodegradable epoxide-containing polyesters from vegetal oils.[26] Moreover, many other biobased polyesters are produced by the lipase-catalyzed polycondensation, e.g., sorbitol-based polyesters,[27, 28] glucose-based polyesters[29] and furan-based polyesters.[30, 31]

Itaconate-based aliphatic polyesters are interesting biobased functional polymers containing carbon-carbon double bonds appending to the polymer main chain.[32-36] These unsaturated aliphatic polyesters are of great interest in biomedical and pharmaceutical fields owing to their biodegradability, biocompatibility, photo-curability and probable bioresorbability.[33] Surprisingly, studies on the synthesis of itaconate-based aliphatic polyesters are scarce.[33, 37-43] We believe this is mainly because the vinyl group of itaconate can be easily deteriorated at elevated temperatures, and the esterification/transesterification reactivity of itaconate is rather low.[40]

Recently, we investigated the CALB-catalyzed polycondensation of biobased succinate, itaconate and 1,4-butanediol.[44, 45] We successfully prepared fully biobased PBS, poly(butylene succinate-*co*-itaconate) (PBSI), and oligo(butylene itaconate) (OBI) via enzymatic polymerization. However, we found that the two-stage enzymatic solution polymerization only resulted in PBSI with a maximum molar percentage of itaconate of around 25 %. In addition, the obtained PBS and PBSI showed similar physical and mechanical properties.

To systematically investigate the two-stage enzymatic polymerization in solution and to enrich the library of saturated and unsaturated aliphatic polyesters, we perform the CALB-catalyzed polycondensation of dimethyl itaconate and 1,4-butanediol with diacid ethyl esters differing in chain length. Various saturated and unsaturated aliphatic polyesters are successfully synthesized via enzymatic polymerization. We investigate the effects of chain length of diacid ethyl ester and the feed ratio of itaconate on the enzymatic polymerization. Moreover, we characterize the chemical structures, molecular weights, crystalline and thermal properties of the obtained aliphatic polyesters, and thermal and mechanical properties of the UV cross-linked unsaturated aliphatic polyesters by NMR, ATR-FTIR, SEC, WAXD, TGA, DSC and tensile test. Furthermore, we discuss the structure-property relationships for the obtained aliphatic polyesters.

Experimental

Materials

The following chemicals were purchased from Sigma-Aldrich: 1,4-butanediol (99+ %); dimethyl itaconate (99 %); diethyl succinate (99 %); diethyl glutarate (99+ %); diethyl adipate (99 %); diethyl sebacate (98+ %); chloroform (HPLC grade); diphenyl ether (99 %); and Lipase B Acrylic Resin from *Candida antarctica* (CALB, in immobilized form as Novozym 435, 5,000+ U/g). Diethyl dodecanedioate (95+ %) was purchased from TCI EUROPE. Diethyl suberate (99 %) was ordered from ABCR. The photoinitiator Irgacure 184 was kindly provided by BASF as a gift.

CALB and diphenyl ether were pre-dried according to the procedures reported in our previous studies.[30, 44, 45] The rest of the chemicals were used as received.

General procedures for CALB-catalyzed synthesis of biobased saturated and unsaturated aliphatic polyesters via a two-stage method in diphenyl ether

The following procedures were applied for the enzymatic polymerization as reported in our previous studies.[44, 45] At first, diesters (diacid ethyl ester and/or dimethyl itaconate, in total 11.10 mmol) and equimolar 1,4-butanediol (1.00 g, 11.10 mmol) were mixed with diphenyl ether (150 wt%) in a round-bottom flask with pre-dried CALB (10 wt%). Then a two-stage method was applied to the enzymatic polymerization. The first stage was performed at 80 °C under a nitrogen atmosphere for 2 h. After that the second stage was carried out at 80 °C under reduced pressure of 2 mmHg for another 94 h.

After the enzymatic polymerization, the obtained products were purified and dried according to the same procedures as described in our previous studies.[44, 45] Finally they were stored in vacuo at room temperature before analysis.

A series of saturated and unsaturated aliphatic polyesters was successfully synthesized via enzymatic polymerization. The following saturated aliphatic polyesters were obtained: poly(butylene succinate) (PBS), poly(butylene glutarate) (PBG), poly(butylene adipate) (PBA), poly(butylene suberate) (PBSu), poly(butylene sebacate) (PBSe) and poly(butylene dodecanedioate) (PBD). The synthetic unsaturated aliphatic polyesters included: poly(butylene succinate-*co*-itaconate) (PBSI), poly(butylene glutarate-*co*-itaconate) (PBGI), poly(butylene adipate-*co*-itaconate) (PBAI), poly(butylene suberate-*co*-itaconate) (PBSuI), poly(butylene sebacate-*co*-itaconate) (PBSeI) and poly(butylene dodecanedioate-*co*-itaconate) (PBDI).

The detailed NMR assignments of the obtained aliphatic polyesters are shown in Tables 1-2.

The ATR-FTIR assignments of the obtained aliphatic polyesters are listed below.

ATR-FTIR (cm^{-1}): 2800 - 3005 (-CH- stretching vibrations), 1710 - 1727 (-C=O stretching vibrations), 1635 - 1640 (asymmetric -C=C- stretching vibrations), 1230 - 1470 (multi-bands, $-CH_2-$ deformation vibrations), 1150 - 1170 (-C-O-C- stretching vibrations), 792 - 815 ($-CH_2-$ rocking vibrations, $-C=CH_2$ twisting vibrations), 710 - 760 ($-(CH_2)_n-$ rocking vibrations).

Table 1. ^{1}H-NMR assignments of the obtained aliphatic polyesters in CDCl$_3$-*d*$_1$.

	^{1}H-NMR, chemical shift (δ, ppm)					
	Butanediol units		**Diacid ethyl ester units**		**Itaconate units**	
Polyester	-O-C***H***$_2$-	-O-CH$_2$-C***H***$_2$-	-CO-C***H***$_2$-	-C***H***$_2$-	=C***H***-	-CO-C***H***$_2$-
PBS	4.11 (m, 4H)	1.70 (m, 4H)	2.62 (m, 4H)			
PBG	4.08 (m, 4H)	1.68 (m, 4H)	2.36 (t, 4H)	1.93 (m, 2H)		
PBA	4.08 (m, 4H)	1.69 (m, 4H)	2.32 (m, 4H)	1.65 (m, 4H)		
PBSu	4.08 (m, 4H)	1.68 (m, 4H)	2.28 (t, 4H)	1.61 (m, 4H); 1.32 (m, 4H)		
PBSe	4.08 (m, 4H)	1.69 (m, 4H)	2.28 (t, 4H)	1.61 (m, 4H); 1.29 (m, 8H)		
PBD	4.08 (m, 4H)	1.69 (m, 4H)	2.28 (t, 4H)	1.60 (m, 4H); 1.27 (m, 12H)		
PBSI	4.05-4.25 (m, 4H)	1.70 (m, 4H)	2.62 (m, 4H)		6.32 (s, 1H); 5.72 (s, 1H)	3.33 (s, 2H)
PBGI	3.98-4.32 (m, 4H)	1.69 (m, 4H)	2.36 (t, 4H)	1.93 (m, 2H)	6.31 (s, 1H); 5.71 (s, 1H)	3.32 (s, 2H)
PBAI	4.02-4.23 (m, 4H)	1.68 (m, 4H)	2.32 (bs, 4H)	1.64 (m, 4H)	6.31 (s, 1H); 5.71 (s, 1H)	3.32 (s, 2H)
PBSuI	3.98-4.33 (m, 4H)	1.69 (m, 4H)	2.28 (t, 4H)	1.61 (m, 4H); 1.32 (m, 4H)	6.31 (s, 1H); 5.71 (s, 1H)	3.33 (s, 2H)
PBSeI	4.01-4.25 (m, 4H)	1.69 (m, 4H)	2.28 (t, 4H)	1.60 (m, 4H); 1.29 (m, 8H)	6.32 (s, 1H); 5.71 (s, 1H)	3.33 (s, 2H)
PBDI	3.98-4.26 (m, 4H)	1.69 (m, 4H)	2.28 (t, 4H)	1.59 (m, 4H); 1.26 (m, 12H)	6.31 (s, 1H); 5.71 (s, 1H)	3.32 (s, 2H)

Table 2. ^{13}C-NMR assignments of the obtained aliphatic polyesters in CDCl$_3$-*d*$_1$.

	^{13}C-NMR, Chemical shift (δ, ppm)							
	Butanediol units		**Diacid ethyl ester units**			**Itaconate units**		
Polyester	-O-***C***H$_2$-	-O-CH$_2$-***C***H$_2$-	-***C***O-	-CO-***C***H$_2$-	-***C***H$_2$-	-***C***O-	=***C***-	-***C***H$_2$-
PBS	64.25	25.31	172.36	29.12				
PBG	64.02	25.39	173.00	33.36	20.22			
PBA	63.97	25.43	173.41	33.98	24.5			
PBSu	63.87	25.46	173.80	34.30	28.92; 24.87			
PBSe	63.85	25.47	173.93	34.40	29.23; 25.05			
PBD	63.84	25.48	173.98	34.44	29.54; 29.39; 29.29; 25.10			
PBSI	64.56; 64.43; 64.23	25.30; 25.28	172.32	29.11		170.70; 166.13	133.92; 128.48	37.74
PBGI	64.62; 64.50; 64.01	25.40; 25.35	173.01	33.37	20.22	170.79; 166.19	133.93; 128.60	37.80
PBAI	64.64; 64.52; 63.96	25.43; 25.36	173.40	33.97	24.5	170.79; 166.19	133.94; 128.58	37.80
PBSuI	64.66; 64.54; 63.88	25.46; 25.37	173.80	34.30	28.92; 24.87	170.80; 166.20	133.95; 128.58	37.80
PBSeI	64.68; 64.55; 63.85	25.47; 25.40	173.92	34.40	29.24; 25.05	170.80; 166.20	134.14; 128.53	37.81
PBDI	64.67; 64.54; 63.83	25.46; 25.39	173.97	34.42	29.53; 29.38; 29.28; 25.08	170.78; 166.19	133.94; 128.56	37.80

Solvent casting of the unsaturated aliphatic polyester films and UV cross-linking

The unsaturated aliphatic polyester (1.5 g) and Irgacure 184 (0.03 g) were dissolved in chloroform (15 mL). Then the solution was poured into a teflon petri dish and covered with aluminum foil, after which chloroform was evaporated at room temperature overnight. The obtained unsaturated polyester film was then placed into a Digital UV/Ozone System (PSD Pro Series, Novascan Technologies, Inc., USA) and irradiated with UV light (185 and 254 nm) for 30 min at 40 °C under nitrogen atmosphere. Finally, the UV cured polyester film was cut to small strips (25 mm × 5 - 6 mm × 0.2 - 0.4 mm) for tensile testing.

Instrumental methods

A Varian VXR spectrometer (^{1}H-NMR, 400 MHz; ^{13}C-NMR, 100 MHz) was used to record spectra of ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H Homonuclear Correlation (COSY), and ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC). The samples were dissolved in CDCl$_3$-d_1. The reported chemical shifts were referenced to the residual solvent resonances of CDCl$_3$-d_1. The molar compositions of the final products were calculated from ^{1}H-NMR spectra according to the method established in our previous reports.[44, 45]

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 ($Đ$, $\overline{M_w}/\overline{M_n}$) were measured at 30 °C on a Viscotek Size Exclusion Chromatography (SEC) system. The SEC was equipped with three detectors and three columns. The detectors were: a LS detector (Viscotek Ralls detector); a VS detector (Viscotek Viscometer Model H502); and a RI detector (Shodex RI-71 Refractive Index detector). The columns included an Agilent guard column (PLgel 5 µm Guard, 50 mm) and two Agilent columns (PLgel 5 µm MIXED-C, 300 mm). The eluent was chloroform (HPLC grade), and the flow rate was 1.0 mL/min. The molecular weights were determined by universal calibration method. The universal calibration curves were generated using narrow polydispersity polystyrene standards (Agilent and Polymer Laboratories). The $\overline{M_w}$ values of the polystyrene standards were ranging from 645 to 3001000 g/mol.

The thermal transitions of the obtained aliphatic polyesters were measured by Differential Scanning Calorimetry (DSC) using a TA-Instruments Q1000. The heating and cooling rate were 10 °C/min. The glass transition temperature (T_g) was also determined by Temperature Modulated DSC (TMDSC) using the same instrument. For the TMDSC test, the heating rate was 2 °C/min, with the temperature modulation of +/- 0.50 °C for every 60 seconds. The TMDSC test started immediately after the normal DSC measurement.

The thermal stability of the obtained aliphatic polyesters was characterized by Thermal Gravimetric Analysis (TGA) on a Perkin Elmer Thermo Gravimetric Analyzer TGA7 under nitrogen atmosphere. The scan rate was 10 °C/min.

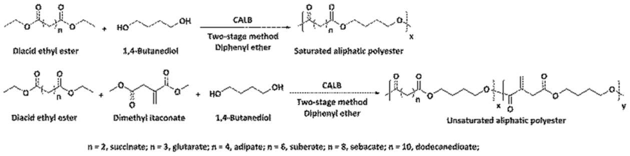
Wide-Angle X-ray Diffraction (WAXD) spectra were recorded at room temperature on a Bruker D8 Advance Diffractometer (Cu Kα_1/Kα_2, λ = 1.54184/1.54056 nm). The degree of crystallinity (χ_c) was determined from the WAXD spectrum according to the method established in our previous reports.[30, 31, 44]

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

Results and discussion

CALB-catalyzed synthesis of biobased saturated and unsaturated aliphatic polyesters via the two-stage method in diphenyl ether

The two-stage enzymatic polymerization of (potentially) biobased diacid ethyl esters, dimethyl itaconate and 1,4-butanediol in diphenyl ether yielded sustainable saturated aliphatic polyesters and itaconate-based unsaturated aliphatic polyesters with different chemical structures, as shown in Scheme 1. The diacid ethyl esters used were: diethyl succinate, diethyl glutarate, diethyl adipate, diethyl sebacate, diethyl suberate, and diethyl dodecanedioate. The number of methylene units between the two carbonyl groups in the tested diacid ethyl esters is 2, 3, 4, 6, 8 and 10, respectively. This number defines the chain length of the tested diacid ethyl esters (n) in this study.



n = 2, succinate; n = 3, glutarate; n = 4, adipate; n = 6, suberate; n = 8, sebacate; n = 10, dodecanedioate;

Scheme 1. CALB-catalyzed synthesis of biobased saturated and unsaturated aliphatic polyesters via a two-stage method in diphenyl ether.

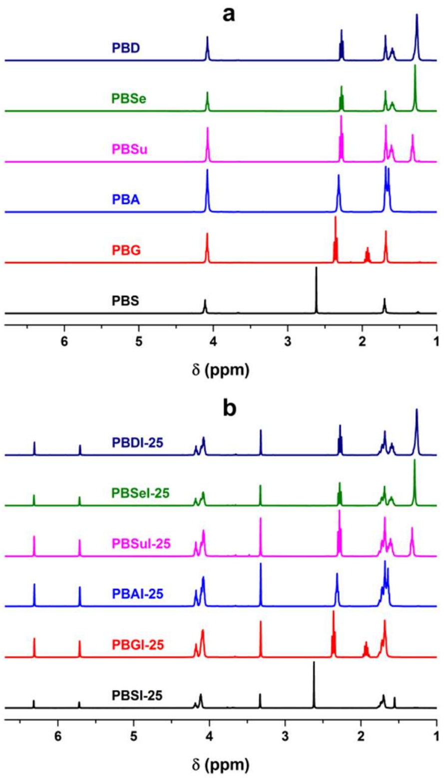


Figure 1. Representative ^{1}H-NMR spectra of the obtained aliphatic polyesters: (a) saturated aliphatic polyesters; and (b) unsaturated aliphatic polyesters containing around 25 % itaconate.

The chemical structures of the obtained aliphatic polyesters were confirmed by NMR and ATR-FTIR (Tables 1-2, Figure 1 and Figures S1-S2 in the Supporting Information). All carbon-carbon double bonds were well preserved after the enzymatic polymerization. As shown in Table 1 and Figure 1b, the two singlets around 5.7 and 6.3 ppm were ascribed to the two vinyl protons in the itaconate units. No extra proton signal was observed, which would have indicated the deterioration of this sensitive group. This is in contrast to the conventional polymerization where itaconate could deteriorate easily through: (1) cross-linking of the carbon-carbon double bonds at elevated temperatures;[33] (2) Michael additions to the carbon-carbon double bonds with alcohol or water;[46] and (3) induced isomerization of itaconate to citraconate or mesaconate by elevated temperatures or some catalysts.[46, 47] However, these side-reactions were successfully prevented during the enzymatic polymerization because of the mild reaction temperature and the catalytic specificity of the enzymes. In conclusion, enzymatic polymerization is a robust approach for the production of polyesters containing sensitive groups.

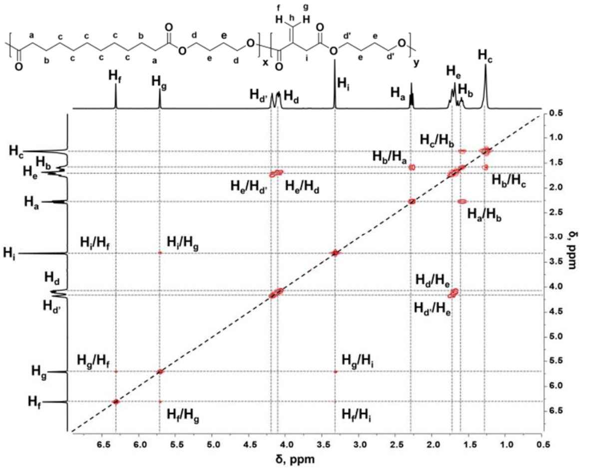


Figure 2. The representative ^{1}H-^{1}H Homonuclear Correlation (COSY) spectrum of poly(butylene dodecanedioate-*co*-itaconate) containing around 25 % itaconate (PBDI-25).

The NMR assignments of the obtained unsaturated aliphatic polyesters were confirmed by 2D NMR: COSY and HSQC. Figure 2 depicts the representative COSY spectrum of poly(butylene dodecanedioate-*co*-itaconate) containing around 25 % itaconate (PBDI-25). The two vinyl proton signals at around 6.3 ppm and 5.7 ppm (H_f and H_g) correlated to each other, and they coupled separately to the methylene proton resonance at around 3.3 ppm (H_i). Therefore, three cross peaks (H_f/H_g, H_i/H_f, and H_i/H_g) appeared in the COSY spectrum, confirming the successfully incorporation of the itaconate units in the co-polyesters. Meanwhile, the methylene protons H_a and H_c coupled separately to another methylene proton H_b from the same dodecanedioate units, showing two off-diagonal peaks H_a/H_b and H_b/H_c in the COSY spectrum. This proves the presence of the dodecanedioate units in the tested PBDI-25. In addition, the similar methylene protons H_d and $H_{d'}$ from the butanediol units showed two resonances at around 4.1 and 4.2 ppm in the ^{1}H-NMR spectra, as they linked to the different acyl groups. The protons H_d were assigned to the methylene protons close to the dodecanedioate units, while the protons $H_{d'}$ were ascribed to the other methylene protons next to the itaconate units. Meanwhile, both of them correlated to another methylene proton H_e within the butanediol units, showing two cross peaks H_e/H_d and $H_e/H_{d'}$. This also suggests the formation of co-polyesters.

Figure 3 illustrates the representative HSQC spectrum of the tested PBDI-25. The successful preservation of the vinyl groups was confirmed by the two cross peaks C_h/H_f and C_h/H_g, where the vinyl carbon resonance at around 128 ppm (C_h) correlated to the two vinyl proton singlets at around 6.3 ppm and 5.7 ppm (H_f and H_g). Meanwhile, the carbon resonance at around 38 ppm (C_i) corresponded to the methylene proton singlet at around 3.3 ppm (H_i). Therefore, the presence of the itaconate units in the co-polyesters was supported by the three cross-peaks C_h/H_f, C_h/H_g and C_i/H_i. In addition, the resonances of the methylene carbons overlapped at around 25 ppm (C_b and C_e) due to the low resolution of the carbon signals in 2D-NMR. However, they split clearly in the standard ^{13}C-NMR spectra, and they corresponded separately to the methylene proton signals at around 1.6 (H_b) and 1.7 ppm (H_e). As shown in Figure 3, the off-diagonal peak C_e/H_e possessed a slightly lower position than that of C_b/H_b. According to this, the carbon resonance at 25.08 ppm was assigned to the methylene carbons C_b from the dodecanedioate units; and the other carbon signals at 25.46 and 25.39 ppm were ascribed to the methylene carbons C_e from the butanediol units. Thus, the cross-peaks C_a/H_a, C_b/H_b and C_c/H_c confirmed the existence of the dodecanedioate units in PBDI; and the off-diagonal peaks $C_{d\&d'}/H_d$, $C_{d\&d'}/H_{d'}$ and C_e/H_e gave the evidence of the butanediol units in the co-polyesters.

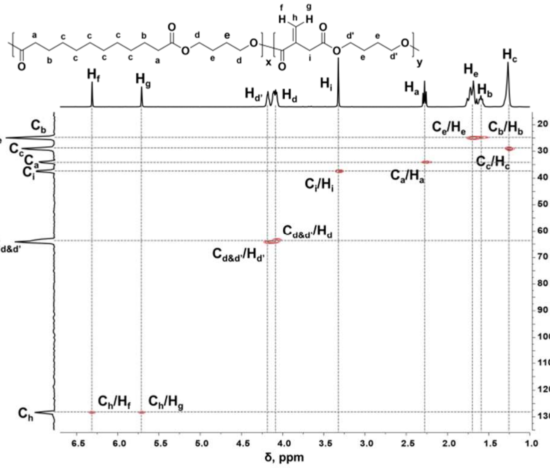


Figure 3. The representative ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) spectrum of poly(butylene dodecanedioate-*co*-itaconate) containing around 25 % itaconate (PBDI-25).

Aliphatic polyesters with the desired chemical compositions were produced from the enzymatic polymerization involving diacid ethyl esters having a chain length of more than 2 (n > 2) (see Table S1 in the Supporting Information). The values of the molar percentage were in good agreement with their feed ratios. As illustrated in Figure 4, the molar percentage of itaconate was tunable from 0 to 35% when using diacid ethyl esters having a chain length of more than 2 (n > 2) in the enzymatic polymerization. In contrast, the molar percentage of itaconate in PBSI matched with the itaconate feed ratios between 0 to 25 % only when using diethyl succinate with the shortest chain length (n = 2) among the tested diacid ethyl esters.[44] By further increasing the feed ratio of itaconate up to 30 % and 35 %, the molar percentage of itaconate dropped significantly to around 15 %. We speculated that this was due to the frequent occurrence of intermolecular transesterifications between the succinate units and itaconate units, as discussed in our previous report.[44] In this case oligomers rich in the itaconate units were produced with low enzymatic reactivity. Thus, the chain growth of these oligomers was greatly hindered, which resulted in lower molecular weights. Besides, the oligomers rich in the itaconate units possessed better solubility in the precipitants (hexane and methanol), and were washed away during the purification step. As a result, only low molecular weight PBSI containing around 15 % itaconate was obtained from the enzymatic polymerization when the feed ratio of itaconate was more than 25 %. However, the intermolecular transesterifications between the diacid ethyl ester units and the itaconate units were greatly suppressed in the enzymatic polymerization involving diacid ethyl esters having a chain length of more than 2 (n > 2), as these diacid ethyl ester units do not match in size with the itaconate units (n = 2). Therefore, the intermolecular transesterifications might have only occurred between the diacid ethyl ester units, which led to the formation of polyester chains with similar enzymatic reactivity. As a result, unsaturated aliphatic polyesters containing the diacid ethyl ester units having a chain length of more than 2 (n > 2) can reach high molecular weights (see Figure 5), and can be easily isolated after purification. In other words, all monomer units were completely incorporated into the polyester chains during the enzymatic polymerization and they were well presented in the purified products. To sum up, the enzymatic polymerization of dimethyl itaconate and 1,4-butanediol with diacid ethyl esters having a chain length of more than 2 (n > 2) yielded aliphatic polyesters with the desirable molar compositions. The molar percentage of itaconate in the final products can be tuned from 0 to 35 % by adjusting the feed ratio of itaconate from 0 to 35 %.

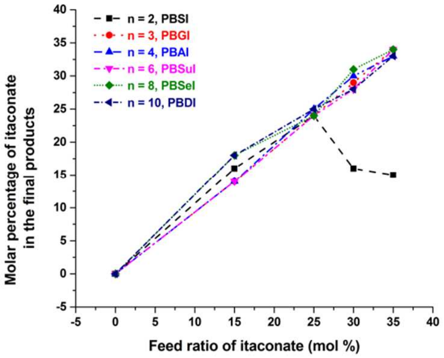


Figure 4. Molar percentage of itaconate (calculated from ^{1}H-NMR) in the final products versus the feed ratio of itaconate.

The chain length of the tested diacid ethyl esters had a significant influence on the molecular weights of the obtained aliphatic polyesters from the enzymatic polymerization. As shown in Figure 5, the enzymatic polymerization with diethyl succinate having the shortest chain length (n = 2) among the tested diacid ethyl esters gave the lowest molecular weights. This is in good agreement with previous studies reported in literature.[24, 48, 49] The enzymatic polymerization with succinate gave the lowest molecular weights compared to those involving diacid derivatives having a chain length of more than 2 (n > 2). This may be due to mainly two reasons. Firstly, the enzymatic reactivity of succinate is quite low, which is caused by its short chain length. Secondly, succinate-based aliphatic polyesters normally possess higher crystallization ability, higher T_m, and lower solubility in the reaction media, compared to the counterparts containing dicarboxylate units having a chain length of more than 2 (n > 2).

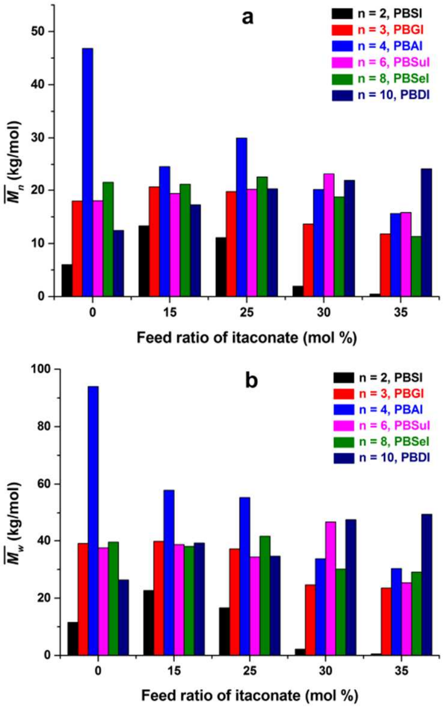


Figure 5. Molecular weights of the obtained aliphatic polyesters from enzymatic polymerization: (a) number average molecular weight ($\overline{M_n}$); and (b) weight average molecular weight ($\overline{M_w}$).

On the other hand, the molecular weights of the obtained aliphatic polyesters containing 0 - 25 % itaconate showed the following trend against the chain length of the tested diacid ethyl esters. The molecular weights increased firstly with increasing chain length of the diacid ethyl esters from 2 to 4. However, further increase of the chain length from 4 to 6, 8 and 10 resulted in lower molecular weights. We found that the enzymatic polymerization of diethyl adipate (n = 4) and 1,4-butanediol with 0 - 25 % dimethyl itaconate gave the highest molecular weights. Similar results were reported by Catalani *el al.*[24] and Papaspyrides *et al.*[50] on the effect of the chain length of dicarboxylic acids/diacid ethyl esters on enzymatic polymerization. Catalani *el al.* studied the CALB-catalyzed azeotropic polymerization of diacid ethyl esters with isosorbide in a mixture of cyclohexane and toluene. They found that the $\overline{M_w}$ of the obtained isosorbide-based polyesters increased significantly from 3000 to 21000 g/mol with increasing chain length of the diacid ethyl esters from 2 to 4. When the chain length were further increased to 6 and 8 the $\overline{M_w}$ decreased to around 9000-10000 g/mol. Papaspyrides *et al.* investigated CALB-catalyzed polymerization of dicarboxylic acids with 1,8-octanediol in diphenyl ether. They found that the product $\overline{M_n}$ (from ^{1}H-NMR) decreased from 8020 to 5360 g/mol when the chain length of dicarboxylic acids increased from 8 to 12. However, they did not give an explanation for these results. We believe this is because CALB shows variable specificity for diacid ethyl esters differing in chain length. As reported by Gotor *et al.*,[51] the CALB specificity constant V_{max}/K_m for the ethyl esters first increased with increasing acyl chain length (the total carbon number in the acryl group) from 2 to 6; then, it decreased similarly when the acyl chain length increased to 8, 10 and 12. Ethyl caproate, which has the same carbon number in the acryl group as diethyl adipate, possessed the highest V_{max}/K_m value. They attributed this to the tighter binding of ethyl caproate to the enzyme. Moreover, Taylor *et al.* investigated the acyl-binding site of CALB.[52] They found that adipic acid was the most preferred substrate among the tested dicarboxylic acids. They explained this by the significantly less entropic component of adipic acid compared to the other tested substrates.

However, it should be noted that enzymatic polymerization is not only affected by the enzyme specificity for the monomers. Many other factors may have influences on enzymatic polymerization, e.g., the solubility of the monomers, the solubility of the polymer, the T_m and the crystallization ability of the final products, the remaining water in the enzymes, and the purity of the monomers. Therefore, we should draw conclusions carefully with respect to the effect of a single factor on enzymatic polymerization. However, given the fact that the polymerization conditions were consistent and the physical properties of the tested diacid ethyl esters and the final products were comparable, we believe that in our case the enzymatic specificity for the tested diacid ethyl esters was the major reason affecting the enzymatic polymerization.

The enzymatic polymerization involving a higher feed ratio of itaconate generally gave lower molecular weights. For instance, the molecular weights of PBAI decreased significantly with increasing feed ratio of itaconate from 0 to 35 %: the $\overline{M_n}$ and $\overline{M_w}$ decreased from 46.8 and 94.0 kg/mol to 15.6 and 30.3 kg/mol, respectively. This is due to the fact that dimethyl itaconate possesses lower enzymatic reactivity compared to all the tested diacid ethyl esters. Therefore, the production of the enzymatic polymerization was dominated by the enzymatic reactivity of dimethyl itaconate. However, the enzymatic polymerization involving diethyl succinate yielded PBS with much lower molecular weights compared to PBSI-15. This can be explained by the higher crystallinity and T_m of PBS, and its lower solubility in the reaction media, as we discussed in our previous studies.[44, 45] Moreover, the enzymatic polymerization involving diethyl glutarate/diethyl suberate/diethyl sebacate resulted in PBGI/PBSuI/PBSeI with similar molecular weights when the feed ratio of itaconate was ranging from 0 to 25 %. The explanations for this phenomena is discussed below. Firstly, phase separation did not occur during the enzymatic polymerization involving diethyl glutarate/diethyl suberate/diethyl sebacate. Secondly, the intermolecular transesterification between the diacid ethyl ester units and the itaconate units was highly suppressed since the glutarate/suberate/sebacate units (n = 3/6/8) do not match in size with the itaconate units. They are longer than the itaconate units (n = 2). Thirdly, CALB may show similar specificity for diethyl glutarate, diethyl suberate and diethyl sebacate.

However, the feed ratio of itaconate showed an opposite effect on the enzymatic polymerization involving diethyl dodecanedioate. The molecular weights of PBDI increased steadily when the feed ratio of itaconate varied from 0 to 35 %: the $\overline{M_n}$ and $\overline{M_w}$ increased from 12.4 and 26.3 kg/mol to 24.2 and 49.5 kg/mol, respectively. This could be explained by two reasons. On one hand, the solubility of PBDI increased with increasing amount of itaconate incorporated into the polyester main chain. Therefore, the phase separation was delayed as more itaconate was incorporated into the polyester main chain. On the other hand, the intermolecular transesterifications between the dodecanedioate units and the itaconate units were extremely suppressed since the dodecanedioate units are 3 times longer than the itaconate units. Therefore, the enzymatic polymerization involving higher ratio of itaconate still gave PBDI with higher molecular weights, although the enzymatic reactivity of all the monomers decreased with increasing feed ratio of itaconate. However, the enzymatic polymerization yielded PBD with much lower molecular weights than that of PBG/PBA/PBSu/PBSe. This can be attributed to the lower solubility and higher crystallization ability of PBD (see the WAXD results later).

Besides, it should be pointed out that the starting building blocks for the enzymatic polymerization are potentially biobased. In this study, their petroleum-based counterparts with high purities were used. However, the biobased chemicals, e.g., succinic acid, usually suffer from inherent impurities such as formic acid and acetic acid.[53, 54] This can alter the quality of the resultant polymers as well as the efficiency of enzymatic polymerization. Therefore, extra purification steps should be employed if those biobased monomers are applied in enzymatic polymerization.

Crystalline properties of the biobased saturated and unsaturated aliphatic polyesters

All the tested saturated aliphatic polyesters were semicrystalline materials, showing the same crystal structures as reported in literature.[55-57] Firstly, the tested PBS crystallized into a monoclinic α-form crystal. It displayed five major diffraction peaks at 2 θ of 19.7 ° (*d* = 4.50 Å, α (020/$\bar{1}$11)), 21.8 ° (*d* = 4.07 Å, α (021)), 22.6 ° (*d* = 3.93 Å, α (110)), 26.1 ° (*d* = 3.41 Å, α ($\bar{1}$21)) and 29.0 ° (*d* = 3.08 Å, α (111)) (see Figure 6a). Secondly, two kinds of crystals were present in the tested PBG and PBA: an orthorhombic β-form (dominant), and a monoclinic α-form (small amount). The tested PBG showed four major diffraction peaks at 2 θ of 21.6 ° (*d* = 4.11 Å, β (110)), 23.6 ° (*d* = 3.77 Å, α (021)), 24.3 ° (*d* = 3.66 Å, β (020)) and 30.0 ° (*d* = 2.98 Å, β (120)). The tested PBA showed four major reflection peaks at 2 θ of 21.4 ° (*d* = 4.15 Å, β (110)), 22.6 ° (*d* = 3.93 Å, α (020)), 24.4 ° (*d* = 3.65 Å, β (020)) and 30.3 ° (*d* = 2.95 Å, β (120)). Thirdly, the tested PBSu, PBSe and PBD all possessed the same orthorhombic crystal structure. They exhibited three characteristic reflection peaks at 2 θ of 21.2 - 21.4 ° (*d* = 4.15 - 4.19 Å, (120)), 24.2 - 24.5 ° (*d* = 3.63 - 3.67 Å, (040)), and 30.1 - 30.3 ° (*d* = 2.95 - 2.97 Å, (140)).

From the WAXD results mentioned above, we can draw the conclusion that the aliphatic polyesters containing more methylene groups in the diacid ethyl ester units prefer to form the orthorhombic crystal structure. This can be explained by the "polyethylene effect": the aliphatic polyester chain approaches that of polyethylene as more methylene units are incorporated into the main chain. Therefore, the crystallization behavior of aliphatic polyesters with more methylene units is similar to that of polyethylene which crystallizes into the same orthorhombic base-centered structure.[58]

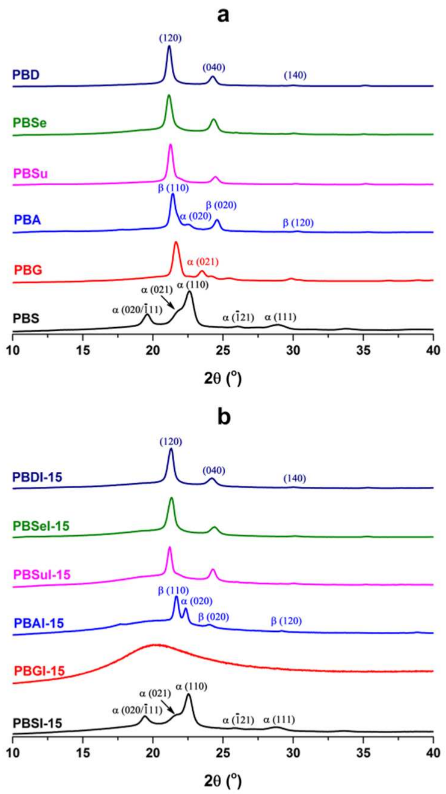


Figure 6. Wide-Angle X-ray Diffraction (WAXD) spectra of the obtained aliphatic polyesters: (a) saturated polyesters; and (b) unsaturated polyesters containing around 15 % itaconate.

The tested PBGI-15 was amorphous at room temperature, showing a broad amorphous halo in its WAXD spectrum (Figure 6b). The other tested unsaturated aliphatic polyesters containing around 15 % itaconate were semicrystalline materials at the same temperature, which adapted the same crystal structures as their saturated aliphatic polyester counterparts.

Among the tested unsaturated aliphatic polyesters containing more than 15 % itaconate, PBGI, PBAI, PBSuI and PBSeI-35 were amorphous at room temperature. The others were semicrystalline materials, including PBSI-25/30/35, PBSeI-25/30 and PBDI-25/30/35 (see Figures S3-S8 in the Supporting Information). PBSeI-25/30 and PBDI-25/30/35 showed the same crystal structures as their saturated aliphatic polyester counterparts. However, the crystal structure of PBSI changed from the monoclinic α-form to the monoclinic β-form when more than 25 % itaconate was incorporated into the polymer main chain. As shown in Figure S3 in the Supporting Information, PBSI containing less than 25 % itaconate crystallized into the monoclinic α-form crystal, while PBSI containing more than 25 % itaconate formed the monoclinic β-form crystal structure. Meanwhile, both of the two crystal structures were identified in PBSI-25. We suspected that the monoclinic α-form crystal was formed by the ordered chain packing between the succinate-butylene-succinate segments which are dominant in PBSI containing less than 25 % itaconate; while the monoclinic β-form crystal was formed by the ordered chain packing between the itaconate-butylene-itaconate segments which are the most abundant microstructures in PBSI containing more than 25 % itaconate. Regarding to PBSI-25, both of these two segments were equally presented.

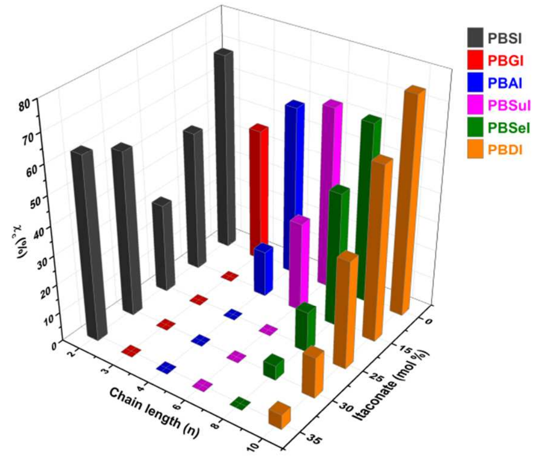


Figure 7. The degree of crystallinity (χ_c) of the obtained aliphatic polyesters against the chain length of the diacid ethyl ester units (n) and the molar percentage of itaconate in the co-polyesters

The degree of crystallinity (χ_c) of the obtained aliphatic polyesters was calculated from the WAXD spectra according to the method established in our previous reports.[30, 31, 44] The results are summarized in Table S2 in the Supporting Information. We found that the chain length of the diacid ethyl ester units had a significant effect on the χ_c value of the tested aliphatic polyesters. The χ_c value first decreased with increasing chain length of the diacid ethyl ester units and then increased with increasing chain length after a threshold (see Figure 7). For example, the χ_c value of the tested saturated polyesters dropped from 69 % to 47 % when the chain length increased from 2 to 3. This is because PBS (n = 2) has a higher chain regularity than PBG (n = 3). Both the succinate units and the diol units in PBS have the same carbon number (4), but the glutarate units (5) in PBG are longer. However, when the chain length increased from 3 to 10, the χ_c value of the saturated aliphatic polyesters increased from 47 % to 71 %. This trend, in which the χ_c value increases with increasing chain length of the diacid ethyl ester units in the polyester main chain, is in good agreement with previous results reported in literature.[59]

Aliphatic polyesters have been found to have increased χ_c values when increasing the methylene numbers in the diester or diol units. We think that this can be attributed to the similar “polyethylene effect” as we discussed above: aliphatic polyesters with more methylene units are similar to polyethylene, which can reach a high degree of crystallinity around 80 - 90%.

The χ_c value of the tested unsaturated polyesters containing diacid ethyl ester units having a chain length of more than 2 (n > 2) decreased significantly with increasing amount of itaconate incorporated into the polyester chain. This can be explained by two reasons: (1) the decrease of chain regularity caused by the chain length difference between the diacid ethyl ester units and the itaconate units; and (2) the hindered effect of the extra appending vinyl groups. However, the χ_c value of PBSI decreased first with increasing molar percentage of itaconate from 0 % to 25 %. Then, it increased when the molar percentage of itaconate further increased from 25 % to 35 %.[44] This is because PBSI containing more than 25% itaconate formed a different crystal structure due to the ordered chain packing between the itaconate-butylene-itaconate segments, as we discussed above. Thus, the chain regularity of PBSI actually increases when more than 25 % of itaconate was incorporated into the main chain.

In conclusion, the crystallization of aliphatic polyesters is significantly affected by the amount of methylene and itaconate units incorporated into the main chain at the tested temperatures and time scales. Generally speaking, aliphatic polyesters (except PBS and PBSI) containing more methylene units or less itaconate units possess higher crystallization ability.

Thermal properties of the biobased saturated and unsaturated aliphatic polyesters

The thermal properties of the obtained aliphatic polyesters were characterized by TGA and DSC. The results are summarized in Table S2 in the Supporting Information.

Figure 8 and Figure S9 depict the representative TGA traces of the tested saturated aliphatic polyesters and unsaturated aliphatic polyesters containing around 35% itaconate. We found that the tested PBS and PBSI possessed relatively lower thermal stability compared to the other tested polyesters. Their decomposition temperature at 5% weight loss ($T_{d\text{-}5\%}$), decomposition temperature at 10% weight loss ($T_{d\text{-}10\%}$), and temperature at maximum rate of decomposition ($T_{d\text{-}max}$) were ranging from 274 to 358 °C, 342 to 374 °C, and 398 to 411 °C, respectively. This might be due to the relatively low molecular weights of PBS and PBSI. The other tested aliphatic polyesters displayed $T_{d\text{-}5\%}$, $T_{d\text{-}10\%}$, and $T_{d\text{-}max}$ at around 350 - 384 °C, 371 - 391 °C, and 414 - 430 °C, respectively. According to the TGA results, we can draw the conclusion that all the tested aliphatic polyesters possess a very broad processing window since they showed high T_d values.

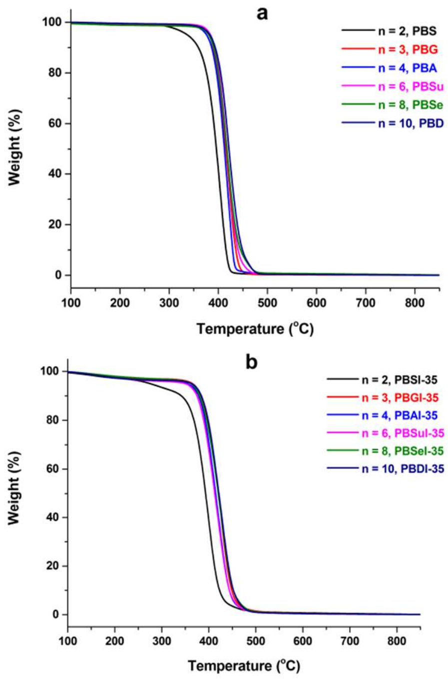


Figure 8. TGA traces of the obtained aliphatic polyesters: (a) saturated aliphatic polyesters; and (b) unsaturated aliphatic polyesters containing around 35 % itaconate.

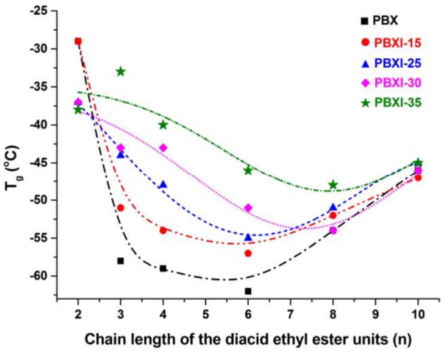


Figure 9. The glass transition temperatures (T_g) of the obtained aliphatic polyesters against the chain length of the diacid ethyl ester units. All T_g values were determined by TMDSC (Temperature Modulated Differential Scanning Calorimetry). PBX represents the tested saturated aliphatic polyesters. PBXI represents the tested unsaturated aliphatic polyesters. The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

The glass transition temperatures (T_g) of the obtained polyesters were determined by DSC and TMDSC (see Table S2). All the tested polyesters showed low T_g values ranging from -65 °C to -25 °C, owing to the high flexibility of the aliphatic chains. We also noticed that the T_g of the tested aliphatic polyesters showed a similar trend with respect to the chain length of the diacid ethyl ester units. As shown in Figure 9, the T_g decreased firstly with increasing chain length of the diacid ethyl ester units from 2 to 6 or 8; then, it increased again when the chain length further increased to 10. We believe this could be explained by the synergistic effects between the flexibility of the polymer main chain and the degree of crystallinity. On one hand, the stiffness of the tested aliphatic polyesters decreases with increasing chain length of the diacid ethyl ester units. This is the major reason attributing to the decrease of T_g with increasing chain length of the diacid ethyl ester units from 2 to 6 or 8. On the other hand, the T_g of the semicrystalline polymers often increases with increasing crystallinity. As discussed above, the degree of crystallinity of the tested aliphatic polyesters increased significantly when the chain length of the diacid ethyl ester units increased to 10.

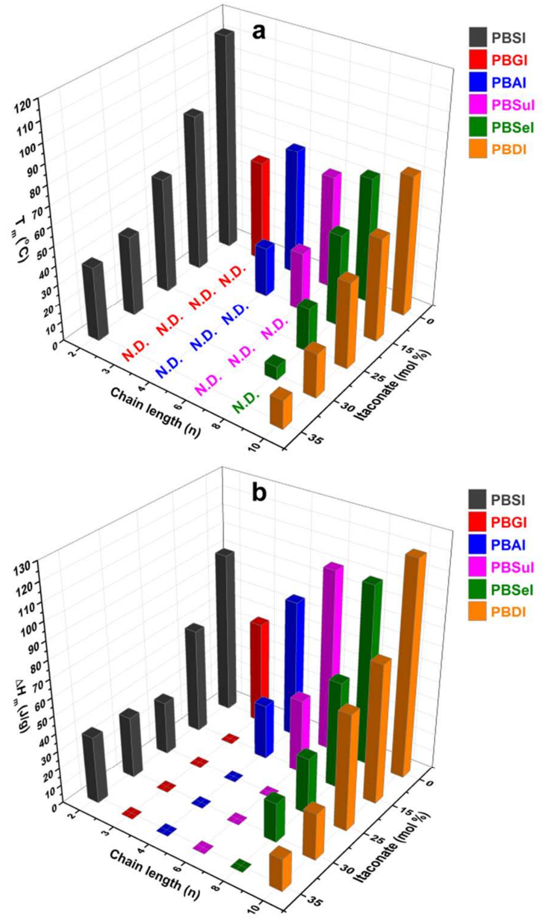


Figure 10. (a) The melting temperatures (T_m, from the first DSC heating scan) and (b) the enthalpies of fusion (ΔH_m, from the first DSC heating scan) of the obtained aliphatic polyesters against the chain length of diacid ethyl ester units and the molar percentage of itaconate. For the tested aliphatic polyesters having multi-melting peaks, the highest T_m is presented here. The symbol N.D. means no melting behavior was detected during the tested time scale.

Figure 10a and 10b depict the melting temperatures (T_m) and enthalpies of fusion (ΔH_m) of the tested aliphatic polyesters against the chain length of the diacid ethyl ester units and the molar percentage of itaconate in the final products. The T_m and ΔH_m showed the following trend with respect to the chain length of the diacid ethyl ester units. They decreased significantly as the chain length of diacid ethyl ester units increased from 2 to 3. However, upon further increasing the chain length from 3 to 10, the T_m and ΔH_m increased steadily again. Meanwhile, the T_m and ΔH_m of the tested aliphatic polyesters containing diacid ethyl ester units having a chain length of more than 2 (n > 2) showed the following trend with respect to the amount of the itaconate units incorporated in the final products. They generally decreased greatly with increasing molar percentage of itaconate in the unsaturated polyesters. Again, the effects of the chain length of diacid ethyl ester units and the molar percentage of itaconate on the thermal transitions of the tested aliphatic polyesters can be explained by the same line of reasoning used in the discussion on crystalline properties.

It should be noted that the T_m, ΔH_m, χ_c of the tested aliphatic polyesters showed the same trend with respect to the chain length of the diacid ethyl ester units and the molar percentage of itaconate (see Figure 7 and Figure 10). This suggests that the WAXD results are in accordance with the DSC results.

Thermal and mechanical properties of the UV cross-linked unsaturated aliphatic polyesters

Solvent casting of the synthetic unsaturated aliphatic polyesters in the presence of UV initiator Irgacure 184 gave uniform and transparent films, except PBSI-15 and PBDI-15 (see Figure S10 in the Supporting Information). The PBSI-15 and PBDI-15 films were opaque since they crystallized during solvent casting. Moreover, the PBSI-15 film cracked after solvent casting, due to the high chain stiffness and crystallization.

The unsaturated aliphatic polyester films were cross-linked by UV light. The carbon-carbon double bonds were consumed after UV radiation. As confirmed by the ATR-FTIR (see Figure S11 in the Supporting Information), the characteristic absorption band ascribed to the carbon-carbon double bonds at 1638 cm^{-1} disappeared after UV cross-linking.

The thermal properties of the UV cured aliphatic polyester films were characterized by DSC, as summarized in Table 3. We found that the T_g of the unsaturated films increased significantly after UV cross-linking, except PBSI-15 which showed the same T_g value before and after UV radiation. This is due to the fact that the PBSI-15 polyester chains were highly restricted by the crystallites before cross-linking; however, they were highly confined by the cross-linked networks after UV curing. We also noticed that the T_g of the cured PBDI-15 was -29 °C, much higher than that of the cured PBSeI-15 (-45 °C), although the polymer chain of PBDI-15 is more flexible. This can be explained by the higher crystallinity of the cured PBDI-15. Moreover, the T_g of the UV cured unsaturated polyester films increased greatly with increasing concentration of the cross-linking moiety in the polymer chains. For instance, the T_g of the cured PBSuI increased significantly from -49 °C to -29 °C when the molar percentage of itaconate increased from 15 % to 35 %. This is reasonable because the cross-linking density increases as more itaconate is incorporated into the cured unsaturated polyesters.

The UV cured PBSI-15, PBSuI-35 and PBDI-35 films were very brittle materials. They possessed values of the Young's modulus and rupture strain of around 106 - 213 MPa and 3 % - 6 %, respectively. The rest of the UV cured unsaturated aliphatic polyester films were more flexible. They showed values of Young's modulus and rupture strain of around 20 - 80 MPa and 10 % - 20 %, respectively. In addition, all the tested UV cured aliphatic polyester films showed similar ultimate tensile stress values around 3 - 6 MPa.

We also found that the UV cross-linked aliphatic polyester films became more brittle as the concentration of the cross-linking moiety increased. This is in good agreement with previous results reported by Yousaf *et al.*.[33] As shown in Table 3, the Young's modulus of the UV cured PBDI increased significantly from around 40 MPA to 213 MPa when the molar percentage of itaconate in PBDI increased from 15 % to 35 %. Correspondingly, the rupture strain decreased greatly from around 19 % to 3 %. Again, this can be explained by the increase of cross-linking density with increasing molar percentage of itaconate in the polyesters.

Table 3. Thermal and mechanical properties of the unsaturated aliphatic polyesters before and after UV cross-linking

	Before UV cross-linking			**After UV cross-linking**					
	DSC [b]			**DSC [b]**			**Tensile test [c]**		
Polymer [a]	**T_m (°C)**	**ΔH_m (J/g)**	**T_g (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**T_g (°C)**	**Young's modulus (MPa)**	**Ultimate tensile Stress (MPa)**	**Rupture strain (%)**
PBSI-15	82	59	-29	91	58	-29	106.3 ± 34.7	3.3 ± 2.2	5.8 ± 4.1
PBSI-25	36, 57 [d]	41	-38	60, 85	31	-32	87.8 ± 17.5	3.7 ± 0.7	5.8 ± 1.9
PBGI-15	/	/	-51	/	/	-39	27.5 ± 4.7	3.0 ± 1.5	12.9 ± 4.9
PBAI-15	26	31	-54	/	/	-39	33.8 ± 2.6	5.8 ± 0.8	19.1 ± 1.9
PBSuI-15	31, 40 [d]	42	-57	/	/	-49	20.4 ± 2.1	3.5 ± 0.5	19.0 ± 3.3
PBSuI-25	/	/	-55	/	/	-34	74.1 ± 7.4	5.6 ± 1.3	11.9 ± 6.8
PBSuI-35	/	/	-46	/	/	-29	139.1 ± 16.8	4.5 ± 1.7	3.9 ± 1.3
PBSeI-15	48	60	-52	/	/	-45	21.5 ± 1.4	4.9 ± 0.8	24.9 ± 3.5
PBDI-15	54	78	-47	61	30	-29	40.5 ± 18.0	4.5 ± 1.1	18.5 ± 4.0
PBDI-25	45	65	-45	/	/	-33	71.2 ± 11.5	5.6 ± 1.7	10.3 ± 4.4
PBDI-35	15	18	-45	/	/	-23	213.1 ± 55.7	4.4 ± 2.8	3.1 ± 2.5

[a] All the tested aliphatic polyesters were produced via the two-stage enzymatic polymerization in diphenyl ether; Uniform films were obtained except PBSI-15; [b] T_m = melting temperature, determined from the first DSC heating scan; ΔH_m = enthalpy of heat fusion, determined from the first DSC heating scan; T_g = glass transition temperature, determined from TMDSC (Temperature Modulated Differential Scanning Calorimetry); / = not detected at the tested time scale; [c] The crosshead speed was 10 mm min^{-1}; [d] Multiple melting temperatures were observed.

Conclusions

Herein we present an environmental-friendly approach for the production of sustainable saturated and unsaturated aliphatic polyesters. In this approach, (potentially) biobased dimethyl itaconate, 1,4-buatnediol and various diacid ethyl esters are used as the building blocks, and CALB is applied as the biocatalyst. We have successfully produced a series of saturated and unsaturated aliphatic polyesters via the two-stage enzymatic polymerization in diphenyl ether. The synthetic aliphatic polyesters reach very high $\overline{M_w}$ values up to 94 kg/mol. They can be used as commodity polymers, thermosetting resins, tissue engineering scaffolds, drug delivery systems, etc.

The enzymatic polymerization involving diacid ethyl esters having a chain length of more than 2 (n > 2) yields high molecular weight polyesters with desirable molar compositions. The molar percentage of itaconate in the unsaturated aliphatic polyesters containing the diacid ethyl ester units having a chain length of more than 2 (n > 2) can be tuned from 0 to 35% by adjusting the feed ratio of itaconate in the enzymatic polymerization. Our results reveal that CALB prefers diacid ethyl esters having a chain length of more than 2 (n > 2); and CALB shows the highest specificity for diethyl adipate (n = 4) among the tested diacid ethyl esters (n = 2 - 10).

Studies on the effects of the chain length of diacid ethyl units on crystalline properties indicates that aliphatic polyesters with the diacid ethyl ester units having a chain length of more than 2 (n > 2) crystallize into the orthorhombic crystal structure. In addition, the unsaturated aliphatic polyesters normally crystallize into the same crystal structure as their saturated aliphatic polyester counterparts.

All obtained aliphatic polyesters possess low T_g values around -60 °C to -25 °C. The T_g of the synthetic aliphatic polyesters first decreases with increasing chain length of the diacid ethyl ester units from 2 to 6 or 8, then increases when the chain length further increases to 10.

The T_m, ΔH_m and χ_c of the synthetic aliphatic polyesters show the same trend with respect to the chain length of the diacid ethyl ester units. They first decrease with increasing chain length of the diacid ethyl ester units from 2 to 3. However, these values increase when the chain length further increases from 3 to 10.

The molar percentage of itaconate in the unsaturated polyesters has the same effect on the T_m, ΔH_m and χ_c of the synthetic aliphatic polyesters. The obtained aliphatic polyesters containing the diacid ethyl ester units having a chain length of more than 2 (n > 2) steadily decrease in T_m, ΔH_m and χ_c with increasing amount of itaconate incorporated into the polyester main chain.

The thermal and mechanical properties of the UV cured itaconate-based polyesters can be controlled by adjusting the chain length of the diacid ethyl ester units and the amount of itaconate units incorporated into the main chain.

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