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Research Article

Aliphatic Polyester Materials from Renewable 2,3-Butanediol

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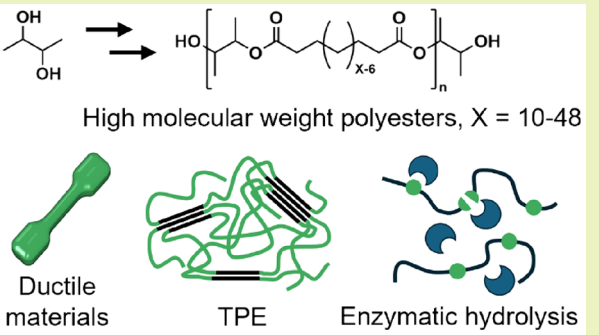
ABSTRACT: 2,3-Butanediol has emerged as a promising bio sourced monomer for polyester synthesis. However, it has received limited attention as monomer for semicrystalline polyesters, due to the lower reactivity of secondary alcohols often resulting in low molecular weight polymers. Furthermore, the methyl branches of 2,3-butanediol reduce the crystallinity of resulting polyesters, leading to lowered melting temperatures. We report the synthesis of semicrystalline polyesters from 2,3-butanediol with long-chain aliphatic dicarboxylate monomers ranging in chain length from C_{10} to C_{48}. With appropriate reaction conditions, high molecular weights up to 59,000 g mol^{-1} were obtained. Polyester-b4.48 (b4 = 2,3-butanediol-based repeat units) features a high melting point of 103 °C and orthorhombic polyethylene-like crystal structure, while shorter dicarboxylate-based polyesters have different crystal structures and polyester-b4.10 is amorphous. Tensile tests of polyester-b4.18 reveal a modulus of elasticity of 290 MPa and elongation at break of 430%. The combination of b4/C_{10} noncrystallizing repeat units with the well-crystallizable C_{48} repeat units provides 2,3-butanediol-based thermoplastic elastomers. Faster enzyme-catalyzed hydrolysis rates were measured for polyester-b4.18 compared to the linear polyester-4.18, indicating an increase in biodegradability with decreasing polymer melting points and crystallinities.



KEYWORDS: *2,3-butanediol, long-chain polyesters, biobased, thermoplastic elastomers*

INTRODUCTION

As an accessible biobased compound, 2,3-butanediol (2,3-BD) is an attractive monomer for polycondensation; however, it is underexplored, essentially due to its low reactivity as a secondary diol compared to petrochemistry based primary diol monomers.[1,2] In contrast to 1,3-propanediol and 1,4-butanediol, 2,3-BD is a natural metabolite produced by numerous bacterial species during fermentation.[1] The microbial production of 2,3-BD can utilize various biomass-derived sources, including xylose, glucose, sucrose, and corn, as well as nonfood resources such as lignocellulose, whey, sugar cane molasses, and crude glycerol.[1,3] Lignocellulose holds great promise as a globally available, cost-effective, and abundant substrate. Lignocellulosic biomass from wood or agricultural residues such as corn cob, corn stover, and apple pomace have been employed for the production of 2,3-BD. The feasibility of industrial scale production of 2,3-BD using lignocellulosic biomasses has been confirmed.[2,4]

Many different species of bacteria can produce 2,3-BD. *Klebsiella pneumoniae*, *Klebsiella oxytoca*, and *Bacillus polymyxa* are among the most efficient microorganisms when it comes to the fermentation to 2,3-BD and can achieve concentrations of 2,3-BD of 150 g L^{-1} with a productivity of 4.21 g L^{-1} h^{-1}.[2,3,5] The pathways for 2,3-BD production in *K. pneumoniae* include the enzymatic conversion of pyruvate to α-acetolactate, which is then converted to acetoin and diacetyl before being transformed into 2,3-BD. The specific stereoisomers of 2,3-BD formed, ((2*S*,3*S*)-BD, (2*R*,3*S*)-BD, or (2*R*,3*R*)-BD), depend on the type of termination enzymes present in the microorganism.[2,6]

2,3-BD has a so far limited utility as monomer in the synthesis of solid polycondensates, one reason being that 2,3-BD reduces or suppresses crystallinity in polyesters.[1,7] For instance, in the synthesis of copolyesters from 1,4-butanediol (1,4-BD), 2,3-BD, succinate, and itaconic acid, 2,3-BD depressed crystallization, leading to a transformation from rigid plastics to soft elastomers with increasing 2,3-BD content.[8] With 2,3-BD as the only diol component, reacted with aliphatic diacids or diesters, amorphous polymers that are liquid at room temperature are formed.[1,9] Therefore, most studies focused on aromatic polymers, coatings, or thermoplastic elastomers (TPEs).[10−14] For instance, low molecular weight polymers from 2,3-BD were used as macromonomers in the synthesis of thermoplastic polyurethanes, blockcopolymers of aliphatic 2,3-BD polyester with PLA as a hard segment were

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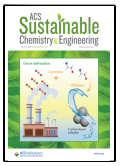

prepared, or resins for coatings were synthesized from 2,3-BD, dimethyl 2,5-furandicarboxylate, and multifunctional comonomers.[12,14,15]

Polyesters from 2,3-BD and many aliphatic diacids with chain lengths up to C_{10} were already reported in 1950 by Watson et al.[9] All obtained polyesters were amorphous resins or balsams, being softer with increasing diacid chain length. Overall, only low number-average molecular weights with a maximum of 2600 g mol^{-1} could be achieved.[9] The low molecular weight is a common attribute of polyesters based on 2,3-BD as only diol component; number-average molecular weights higher than 10,000 g mol^{-1} are exceptions.[11,15,16] This is a result of the low reactivity of secondary alcohols.[10,12,17] In a kinetic study comparing the reactivity of 1,4- and 2,3-BD with adipic acid, it was found that the esterification rate was 6−10 times higher with 1,4-BD at the conditions employed. This is reflected in the molar masses; only a M_n = 5600 g mol^{-1} could be obtained for polyester from 2,3-BD after 5 h of polymerization, whereas for polyester prepared from 1,4-BD a M_n = 31,200 g mol^{-1} was found after an identical reaction time.[1] These low molecular weights together with the low melting temperatures in aliphatic polymers limit mechanical properties and applications of polyesters from the secondary diol 2,3-BD. To our knowledge, there is no report on aliphatic polyesters with 2,3-BD as only alcohol component that resembled solid materials with suitable mechanical properties at ambient temperature.

Studies of isosorbide, another biobased secondary diol that faces similar problems of low reactivity and low molecular weights, are instructive. Isosorbide can be gained by hydrolysis of polysaccharides followed by hydrogenation and subsequent dehydration of the sorbitol intermediate and it is produced on an industrial level.[18,19] To improve the reactivity and thus the polymer molecular weights, various strategies were applied, such as transforming the hydroxy groups into more reactive functionalities, using catalytic amounts of acetic anhydride or forming reactive aryl esters by using aryl alcohols as the reactive solvent.[20−23] Due to its molecular rigidity, bulkiness, and chirality, isosorbide leads to a depression of crystallinity and an increase in glass transition temperature when used in polyesters.[18,19,21,24,25] These high glass transition temperatures in isosorbide polyesters lead to solid materials at room temperature, in contrast to 2,3-BD based aliphatic polyesters that are usually liquid at room temperature.

An approach to obtain polyesters from 2,3-BD that are solid at room temperature without including aromatic monomers can be the introduction of crystallizable segments via long-chain aliphatic dicarboxylate repeat units. A polyester from 1,12-dodecanedioic acid and 2,3-BD was reported to melt at −12 °C, illustrating that significantly longer methylene sequences are required. Notably, the melting temperature of the corresponding polyester from ethylene glycol was 78 °C, illustrating the strong suppression of the melting temperature by branched 2,3-BD-derived repeat units.[15] Long-chain aliphatic monomers can be produced from fatty acids from renewable resources such as seed or microalgae oils via catalytic processes.[26] Self-metathesis of unsaturated fatty acids followed by hydrogenation of the double bond results in α,ω-difunctional monomers, such as 1,18-octadecanedioic acid from oleic acid and 1,26-hexacosanedioic acid from erucic acid.[27−29] Alternatively, 1,18-octadecanedioic acid is also available from enzymatic ω-oxidation of plant oil feedstocks.[30] Palladium-catalyzed isomerizing alkoxycarbonylation allows for the linear incorporation of the entire chain, giving 1,19-nonadecanedioic acid from oleic acid and 1,23-tricosanedioic acid from erucic acid.[31−33] By combination of olefin metathesis and dynamic catalytic isomerizing crystallization, ultralong-chain monomers, such as 1,48-octatetracontanedioic acid, can be accessed.[34] Polyesters from these monomers and linear diols show polyethylene-like properties, reflected in their relatively high melting temperature and the orthorhombic crystal structure as well as tensile properties. These similarities are based on the van der Waals interactions between adjacent hydrocarbon chain segments, which are the predominant forces in HDPE as well as in long-chain aliphatic polyesters.[35]

We now report on semicrystalline thermoplastic ductile polyesters and thermoplastic elastomers derived from 2,3-butanediol (2,3-BD) and long-chain aliphatic dicarboxylic monomers.

EXPERIMENTAL SECTION

Materials. All reactions with moisture- and air-sensitive substances were performed under an inert gas atmosphere using standard Schlenk or glovebox techniques. 2,3-Butanediol (mixture of stereoisomers, ∼ 75% of meso-isomer and ∼25% of D-/L-isomer according to ^{1}H NMR spectroscopic analysis), 1,11-undecanedioic acid (C_{11} diacid), dimethyl 1,12-dodecanedioate (C_{12} diester), 1,13-tridecanedioic acid (C_{13} diacid), and 1,20-eicosanedioic acid (C_{20} diacid) were purchased from TCI chemicals. Titanium(IV) butoxide, dibutyltin oxide (DBTO), sebacic acid (C_{10} diacid), dimethyl sebacate (C_{10} diester) and 1,4-butanediol were purchased from Sigma-Aldrich. Ethylene glycol was purchased from Carl Roth. 1,14-Tetradecanedioic acid (C_{14} diacid) was obtained from Cathay Industrial Biotech, Ltd. 1,15-Pentadecanedioic acid (C_{15} diacid) was purchased from Carbosynth Ltd. 1,16-Hexadecanedioic acid (C_{16} diacid) was purchased from abcr GmbH. 1,17-Heptadecanedioic acid (C_{17} diacid) and 1,21-heneicosanedioic acid (C_{21} diacid) were obtained from BLD Pharmatech GmbH. 1,18-Octadecanedioic acid (C_{18} diacid) was purchased from Elevance Renewable Sciences, Inc. Dimethyl 1,18-octadecanedioate (C_{18} diester), dimethyl 1,19-nonadecanedioate (C_{19} diester), dimethyl 1,23-tricosanedioate (C_{23} diester), dimethyl 1,26-hexacosanedioate (C_{26} diester), and dimethyl 1,48-octatetracontanedioate (C_{48} diester) were synthesized according to reported procedures.[34,36−38]

Polycondensation Procedure I: Smaller-Scale Synthesis. For screening of their thermal properties, polyesters were synthesized on a gram scale in glass inlets equipped with a magnetic stir bar and placed in a heating block fitted into a custom-made stainless steel vessel. The inlets were each charged with 1.0 g of C_X diacid or diester (X = 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 23, 26, 48; 1.0 equiv), 2,3-BD (2.5 equiv), and DBTO (1.0 mol %), the vessel housing the metal block with the inlets was closed, and the reactor was flushed with an inert atmosphere. The mixtures were stirred at 150 °C for 2 h at atmospheric pressure and at 180 °C for 16 h at 800 mbar. The pressure was reduced to 100 mbar for 30 min, to 10 mbar for another 30 min and finally to 0.4 mbar for 24 h. All polymers were characterized as received without further workup. The received polyesters are designated as PE-b4.X, where "b4" represents 2,3-BD ("b" for branched, "4" for the number of carbon atoms of 2,3-BD) and "X" represents the chain length, i.e., number of carbon atoms of the diester/diacid monomer, e.g. a polyester from C_{18} diacid or diester and 2,3-BD is termed PE-b4.18.

Polycondensation Procedure II: Larger-Scale Synthesis of PE-b4.18. Dimethyl 1,18-octadecanedioate (20.00 g, 58.39 mmol, 1.0 equiv) and DBTO (0.15 g, 0.58 mmol, 1.0 mol %) were degassed in a 250 mL round-bottom flask. 2,3-BD (13.03 mL, 145.98 mmol, 2.5 equiv) was added, and the mixture was stirred at 150 °C for 2 h and at 180 °C for 19 h. To remove residual 2,3-BD, the pressure was reduced to 800 mbar for 2.5 h, to 100 mbar for 0.5 h, and to 10 mbar for 1.5 h. Polymerization was then continued at 0.05 mbar, for 32 h at 180 °C and for 3 h at 220 °C. The white PE-b4.18 formed was used as

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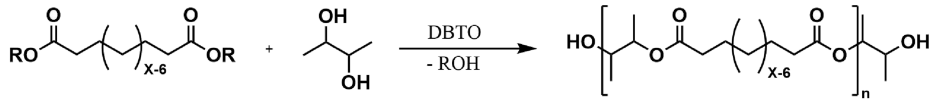
Scheme 1. Synthesis of Polyesters PE-b4.X[a] from 2,3-BD[b] as Diol and a Long-Chain Aliphatic Diacid or Diester



R = H, Me
X = 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 23, 26, 48

[a]"b": branched, "4": number of carbon atoms of 2,3-BD, "X": chain length, i.e., number of carbon atoms of the diester/diacid monomer, X = 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 23, 26, 48. [b]Mixture of stereoisomers.

received without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ [ppm] = 4.99 (m, $(CH_3)CHO$), 4.86 (m, end group $(CH_3)CHO$), 3.88 (m, end group $(CH_3)CHOH$), 3.74 (m, end group $(CH_3)CHOH$), 3.66 (s, end group OCH_3), 2.28 (m, $CH_2C(O)O$), 1.60 (m, $CH_2CH_2C(O)O$), 1.29 (m, backbone CH_2), 1.17 (s, $CHCH_3$).

Polycondensation to Thermoplastic Elastomer PE-b4.10/48. Dimethyl sebacate (15.67 g, 68.04 mmol, 0.923 equiv), dimethyl 1,48-octatetracontanedioate (4.33 g, 5.67 mmol, 0.077 equiv), and DBTO (0.18 g, 0.74 mmol, 1.0 mol %) were degassed in a 250 mL round-bottom flask. 2,3-BD (16.44 mL, 184.3 mmol, 2.5 equiv) was added, and the mixture was stirred at 150 °C for 2 h and at 180 °C for 23 h. To remove residual 2,3-BD, the pressure was slowly reduced to 10 mbar over 3 h, and polymerization was continued at 0.05 mbar for 5 days. The received polymer is designated PE-b4.10/48, with "b4" representing 2,3-BD and 10/48 indicating that it is a copolymer from C_{10} and C_{48} diester. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ [ppm] = 4.97 (m, $(CH_3)CHO$), 4.79 (m, end group $(CH_3)CHO$), 3.88 (m, end group $(CH_3)CHOH$), 3.74 (m, end group $(CH_3)CHOH$), 3.66 (s, end group OCH_3), 2.28 (m, $CH_2C(O)O$), 1.60 (m, $CH_2CH_2C(O)O$), 1.29 (m, backbone CH_2), 1.17 (s, $CHCH_3$).

METHODS

NMR spectra were recorded on a Bruker Avance III 400 or a Bruker Avance II HD 400 spectrometer. ^{1}H chemical shifts were referenced to the residual solvent signals. Data processing and analysis was carried out using MestReNova software.

Differential scanning calorimetry (DSC) analyses were performed on a Netzsch DSC 204 F1 Phoenix instrument with heating and cooling rates of 10 K min^{-1} in closed 40 μL alumina pans under a nitrogen atmosphere (software: Netzsch Proteus Thermal Analysis, version 6.1.0).

Wide-angle X-ray scattering (WAXS) diffractograms were recorded on a D8 Discover instrument (Bruker) with Cu–Kα radiation and a Vantec or LynxEye detector.

Gel permeation chromatography (GPC) was performed on a SECurity^2 GPC system from Polymer Standards Service (PSS) with a SDV Linear M 5 μm column with IR and UV/Vis detection. The samples were measured in chloroform at 35 °C. Molecular weights were determined versus narrow polystyrene standards. High-temperature GPC was performed on a PolymerChar GPC-IR instrument equipped with an integrated viscometer and an IR5 infrared detector on PSS POLEFIN Linear XL columns (3 × 30 cm, additional guard column) at 160 °C in 1,2-dichlorobenzene with a flow rate of 1 mL min^{-1}. Molecular weights were determined versus narrow polystyrene standards. The raw data was evaluated with PSS WinGPC software.

Dog bone-shaped specimens, according to ISO527–2, type 5A, were prepared using a Micro Compounder (15 mL) by XPLORE and injected into a Micro Injection Molder by XPLORE with a shot volume of 5.5 mL (IM 5.5). Tensile testing was performed on the injection molded specimens preconditioned at room temperature for 24 h. The experiments were performed on a Zwick Z005/1446 Retroline tC II machine with a clamping length of 50 mm and a crosshead speed of 5 mm min^{-1}. Data analysis was performed using the software Zwick Roell testXpert II.

For cyclic hysteresis tests, the test specimens underwent repeated cycles of loading and unloading to a strain of 100% and a crosshead speed of 50 mm min^{-1}. To evaluate the recovery, the residual strain was observed after 10 cycles.

For enzymatic hydrolysis experiments, melt pressed films were prepared by heating polymer in a 9 cm diameter press mold at 150 °C followed by cooling to room temperature under 10 kN hydraulic pressure. From these larger films, smaller specimens (1 cm diameter) were cut out. For each incubation, 5 or 6 small films (20–25 mg total mass) were employed.

Enzymatic hydrolysis incubations were performed similarly as in previously reported protocols.[39,40] Glass vessels were used, which had ground joints to hold a combined pH/temperature probe, a buret for base addition, and a N_2 feed to minimize ingassing of CO_2 into the test solution. To each vessel, 200 μL of cutinase solution (cutinase from *Humicola insolens*, product Novozymes 51032; ChirvalVision, NL) was added to 100 mL of 10 mM KCl buffered by 100 μM phosphate buffer (pH 7.0). The incubation time began upon addition of the polymer films to the solution. Throughout, the solution temperature was controlled by an external circulating water bath and monitored by a Pt1000 temperature probe integrated into the pH electrode. For PE-b4.18 and PE-4.18, 30 °C was used, while 40 °C was used for PE-b4.26. The solution pH was held constant at 7.0 by automatic titration of 10 mM KOH from Dosino 800 dosing units controlled by a Titrando 907 titration device (Metrohm, CH).

RESULTS AND DISCUSSION

Synthesis of Polyesters from 2,3-Butanediol and Long-Chain Aliphatic Monomers (C_{10}–C_{48}). 2,3-Butanediol (2,3-BD) was reacted with a range of mid- and long-chain aliphatic diacids or diesters to polyesters to elucidate the impact of different repeat unit chain lengths on the crystal structure, crystallinity, and thermal properties of the polyesters.

In a series of smaller-scale reactions, 2,3-BD was reacted with sebacic acid (C_{10} diacid), 1,11-undecanedioic acid (C_{11} diacid), dimethyl 1,12-dodecanedioate (C_{12} diester), 1,13-tridecanedioic acid (C_{13} diacid), 1,14-tetradecanedioic acid (C_{14} diacid), 1,15-pentadecanedioic acid (C_{15} diacid), 1,16-hexadecanedioic acid (C_{16} diacid), 1,17-heptadecanedioic acid (C_{17} diacid), dimethyl 1,18-octadecanedioate (C_{18} diester), dimethyl 1,19-nonadecanedioate (C_{19} diester), 1,20-eicosanedioic acid (C_{20} diacid), 1,21-heneicosanedioic acid (C_{21} diacid), dimethyl 1,23-tricosanedioate (C_{23} diester), dimethyl 1,26-hexacosanedioate (C_{26} diester), and dimethyl 1,48-octatetracontanedioate (C_{48} diester), respectively, to investigate the influence of different chain lengths under comparable conditions (Scheme 1). A reaction temperature of 180 °C was chosen, as the reaction rate of secondary alcohols is highly temperature dependent and increases significantly with increasing temperature.[1] Number average molecular weights (M_n) of the obtained polyesters ranged from 7500 to 44,700 g mol^{-1} as determined by GPC analysis measured vs polystyrene standards (Table 1). Molecular weights from ^{1}H NMR were determined by end group analysis. Note that the difference between NMR and GPC nominal values results from the difference in hydrodynamic behavior of the polyesters studied

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Table 1. All Synthesized PE-b4.X Polyesters and Their Molecular Weights

polymer	monomer	M_n (NMR) [10^3 g mol^{-1}][c]	M_n (GPC) [10^3 g mol^{-1}][d]	M_w (GPC) [10^3 g mol^{-1}][d]	$Đ$
PE-b4.10	C_{10} diacid	10.1	20.0	36.3	1.8
PE-b4.11	C_{11} diacid	12.1	22.1	41.8	1.9
PE-b4.12	C_{12} diester	12.4	23.7	44.9	1.9
PE-b4.13	C_{13} diacid	11.9	27.1	50.2	1.9
PE-b4.14	C_{14} diacid	15.1	27.5	52.2	1.9
PE-b4.15	C_{15} diacid	8.3	15.6	31.7	2.0
PE-b4.16	C_{16} diacid	14.6	32.3	62.6	1.9
PE-b4.17	C_{17} diacid[b]	23.7	44.7	121.0	2.7
PE-b4.18	C_{18} diester	11.7	18.2	31.8	1.7
PE-b4.18[a]	C_{18} diester	34.8	59.0	135.1	2.3
PE-b4.18[a]	C_{18} diester	35.0	48.7	106.5	2.2
PE-b4.19	C_{19} diester	5.1	7.9	15.7	2.0
PE-b4.20	C_{20} diacid[b]	34.8	37.4	88.9	2.4
PE-b4.21	C_{21} diacid	17.2	39.2	105.3	2.7
PE-b4.23	C_{23} diester	6.2	8.3	17.0	2.1
PE-b4.26	C_{26} diester	4.5	7.5	14.7	2.0
PE-b4.48	C_{48} diester	8.8	9.0	17.5	1.9

[a]Synthesis according to 'Polycondensation procedure II'. [b]Only 0.5 g of diacid used instead of the usual 1 g. [c]Determined by ^{1}H NMR end group analysis. [d]Determined by GPC vs polystyrene standards in $CHCl_3$ at 35 °C, except for PE-b4.48 which was analyzed vs polystyrene standards in 1,2-dichlorobenzene at 160 °C.in 1,2-dichlorobenzene at 160 °C.

in comparison to polystyrene, which is used for calibration of GPC.

PE-b4.18 was synthesized on a comparatively larger scale with the objective of achieving high molecular weights for evaluation of the mechanical properties. In order to obtain high molecular weight polyesters from the secondary 2,3-BD, we determined that a high conversion of the methyl ester groups of the monomers during the initial oligomerization step is crucial. An excess of 2.5 equiv of 2,3-BD was used to facilitate high conversions of the methyl ester to the ester with 2,3-BD. In preliminary experiments, we found that one reason for low molecular weights was the removal of excess 2,3-BD due to premature applying of reduced pressure, resulting in the absence of hydroxyl end groups available to react with remaining methyl ester groups. Therefore, the progress of the transesterification reaction was monitored by ^{1}H NMR spectroscopy, specifically tracking the intensity of the signal at 3.66 ppm, which corresponds to the methyl end groups of the diester (cf. Figure S2). With proceeding reaction, the methyl ester group intensity decreased. The reaction was continued, until only 15% of the original methyl groups remained, while still ensuring an excess of hydroxyl end groups.

In the subsequent polymerization step, the excess 2,3-BD was removed under reduced pressure. The reaction progress and increase in molecular weight was monitored through gel permeation chromatography (GPC) measurements (cf. Table S1). The reaction proceeded, until a high molecular weight PE-b4.18 was reproducibly obtained (M_n = 49,000 g mol^{-1} and M_n = 59,000 g mol^{-1}, respectively, in two independent experiments).

Using [Ti(OBu)$_4$] as an alternative catalyst also yielded high molecular weight polymers, with number average molecular weights of 20,000 g mol^{-1}. A direct comparison revealed that dibutyltin oxide (DBTO) exhibited faster reactivity, resulting in higher molecular weights within the same reaction time (cf. Table S2). We also compared the polycondensation of C_{18} diester and C_{18} diacid. The C_{18} diester was initially chosen, as the oligomerization can be monitored using ^{1}H NMR spectroscopy in contrast to the C_{18} diacid, where the end group signal $-CH_2COOH$ at 2.30 ppm overlaps with the backbone signal $-CH_2COO-$ at 2.28 ppm. A comparison between C_{18} diester and C_{18} diacid monomers demonstrated that both exhibit similar reaction rates and lead to molecular weights exceeding 40,000 g mol^{-1} after a polymerization time of 35 h (cf. Figure S5). Additionally, we compared the oligomerization process of 2,3-BD and ethylene glycol (EG) with C_{18} diester. The primary diol EG exhibited a significantly faster reaction rate compared to 2,3-BD (cf. Figure S7). After 10 h, only 2% of methyl end groups remained in the EG oligomers whereas for the secondary diol, 28% of methyl end groups persisted. This behavior aligns with comparable systems reported previously.[1]

Thermal properties and crystal structure. DSC measurements showed that melting points increase continuously with increasing length of the dicarboxylate repeat units (Table 2). PE-b4.10 and PE-b4.11 were found to be fully

Table 2. Melting Temperature T_m, Crystallization Temperature T_c, Melting Enthalpy ΔH_m, and Crystallinity χ of Polymers Obtained from 2,3-BD with Diesters or Diacids with Different Chain Lengths

polymer	M_n (GPC) [10^3 g mol^{-1}]	T_m [°C][a]	T_c [°C][a]	ΔH_m [J g^{-1}][a]	χ [%][b]
PE-b4.10	20.0				
PE-b4.11	22.1				
PE-b4.12	23.7	−18	−34	22	
PE-b4.13	27.1	−6	−20	35	
PE-b4.14	27.5	11; 42	−5	42	n.d.
PE-b4.15	15.6	19; 48	9	52	n.d.
PE-b4.16	32.3	29; 53	18	55	n.d.
PE-b4.17	44.7	35	24	58	n.d.
PE-b4.18	18.2	45	35	66	37
PE-b4.19	7.9	50	38	80	43
PE-b4.20	37.4	52	41	65	n.d.
PE-b4.21	39.2	56	44	69	n.d.
PE-b4.23	8.3	64	55	92	49
PE-b4.26	7.5	75	65	107	60
PE-b4.48	9.0	103	91	147	72

[a]Determined by DSC (10 K min^{-1}). [b]Calculated from WAXS.

amorphous and PE-b4.12 has a low melting temperature, resulting in viscous liquids at room temperature. PE-b4.14, PE-b4.15 and PE-b4.16 showed two distinct melting peaks, with the one at lower temperature having the larger area. The longer chain polymers were obtained as white solids at room temperature, with melting points up to 103 °C for PE-b4.48. This trend can be attributed to the reduced influences of the functional groups, in this case ester and methyl side chain groups, with increasing chain length. Furthermore, the melting enthalpy is increasing from 22 J g^{-1} in PE-b4.12 to 147 J g^{-1} in PE-b4.48, which indicates a higher degree of crystallinity for polymers from longer chains. Slight fluctuations in this trend are attributed to differences in molecular weight.

Comparing the methyl branched PE-b4.X polyesters derived from 2,3-BD with linear PE-2.X polyesters from ethylene glycol (EG),[41] the 2,3-BD polyesters generally exhibit lower melting

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temperatures with similar diester/diacid monomer chain length (Figure 1). As the monomer chain length increased,

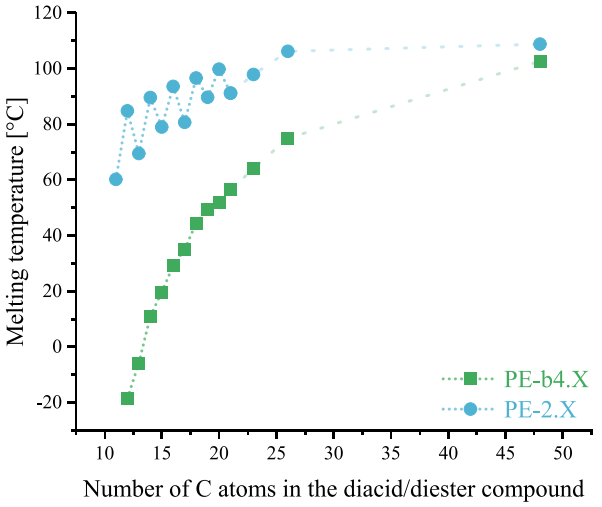

Figure 1. Melting temperatures of PE-b4.X (from 2,3-BD) and PE-2.X (from ethylene glycol (EG)) for reference.[41] Dotted lines are merely a guide to the eye.

the melting temperatures of both types of polyesters approach each other, resulting in only minor differences between PE-b4.48 and PE-2.48, with values of 103 and 109 °C, respectively. A significant odd−even effect was found in the PE-2.X polyesters, which was absent in the PE-b4.X polyesters. This behavior shows that in PE-2.X polyesters, the ester groups have the main effect on the resulting melting temperatures, leading to a depression in melting temperature by incorporation into the crystal lattice and to the odd−even effect, which is based on matched or mismatched dipole−dipole interactions between ester groups. This is different in PE-b4.X, where the more sterically demanding methyl groups are incorporated in the crystal and lead to more significant packing defects than the ester groups.[42] Therefore, the melting temperature is more depressed when methyl groups are part of the polyester crystal. In addition, the ability of the ester groups to form dipole−dipole interactions is suppressed and the odd−even effect is absent.

The polymers with dicarboxylate monomer chain lengths from C_{18} to C_{26} exhibit a pseudohexagonal crystal structure, indicated by the single reflection at 21.5° in wide-angle X-ray scattering (WAXS) studies (Figure 2).[43,44] However, with longer monomer chains, resulting in a lower concentration of methyl branching, a transition occurs in PE-b4.48, where two reflections are detected, at 21.6° and at 23.8°. This indicates an orthorhombic crystal structure, which is also observed in linear polyesters such as PE-2.18.[45] A similar transition from a pseudohexagonal to an orthorhombic crystal structure with decreasing number of methyl side chains has been observed in ethylene-propylene copolymers. In copolymers with high ethylene content (>65 wt %), an orthorhombic crystal structure is observed, while lower ethylene content leads to the formation of a pseudohexagonal structure, which can incorporate the propene units into the unit cells. This incorporation of methyl groups results in a high degree of structural disorder, leading to decreased melting temperatures and crystallinity.[46,47] Similarly, it is hypothesized that in the PE-b4.X polymers, with monomer chain lengths up to C_{26}, the

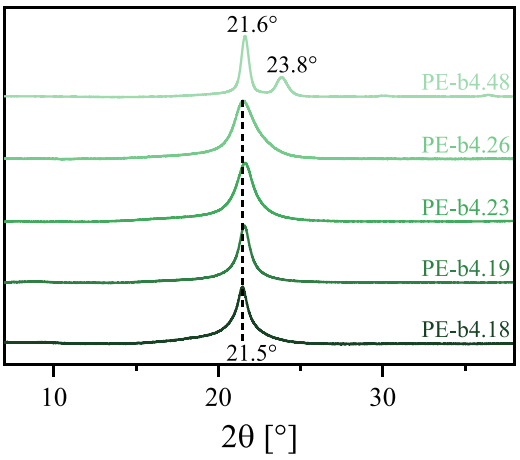

Figure 2. WAXS diffractograms of PE-b4.18, PE-b4.19, PE-b4.23, and PE-b4.26, showing reflections at 21.5°, indicating a pseudohexagonal crystal structure and PE-b4.48 with reflections at 21.6° and 23.8°, having an orthorhombic crystal structure.

methyl groups from 2,3-BD are integrated into the crystals, explaining the preference for pseudohexagonal crystallization. The crystallinity values derived from WAXS are consistent with the trend found for melting enthalpies obtained from DSC. The crystallinity of PE-b4.18 was determined as $\chi \approx 37\%$, and it gradually increased with increasing monomer chain length, ultimately reaching $\chi \approx 72\%$ in PE-b4.48.

Mechanical Properties of PE-b4.18. The upscaled high molecular weight polyester PE-b4.18 with number-average molecular weight of 49,000 g mol^{-1} was investigated regarding its tensile properties. After compounding and injection molding processes to produce dog bone specimens, the polymer had a molecular weight of M_n = 41,000 g mol^{-1}.

Investigation of the mechanical properties of the material by stress−strain measurements of injection molded specimens gave a Young's modulus (E_t) of 290 MPa, yield strength (σ_y) of 10.8 MPa, and elongation at break (ε_{tb}) of 430% for PE-b4.18 (Figure 3 and Table S3). The material shows a lower

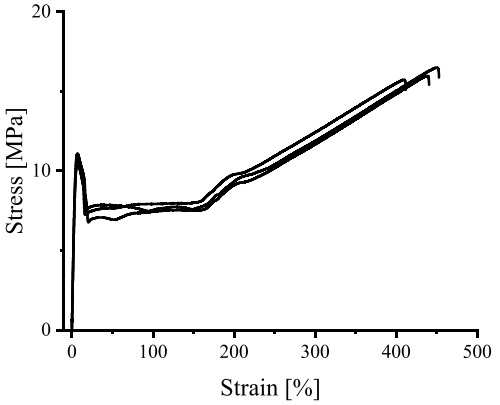

Figure 3. Stress−strain curves of injection-molded PE-b4.18.

modulus of elasticity and yield strength, but higher ductility compared to PE-2.18 (E_t = 730 MPa, σ_y = 19 MPa, ε_{tb} = 330%).[45] The reduced crystallinity, resulting from the presence of methyl branches, can account for these differences. The observed properties are in the range of properties found for LDPE (E_t = 240 MPa, σ_y = 12 MPa, ε_{tb} = 653%).[48]

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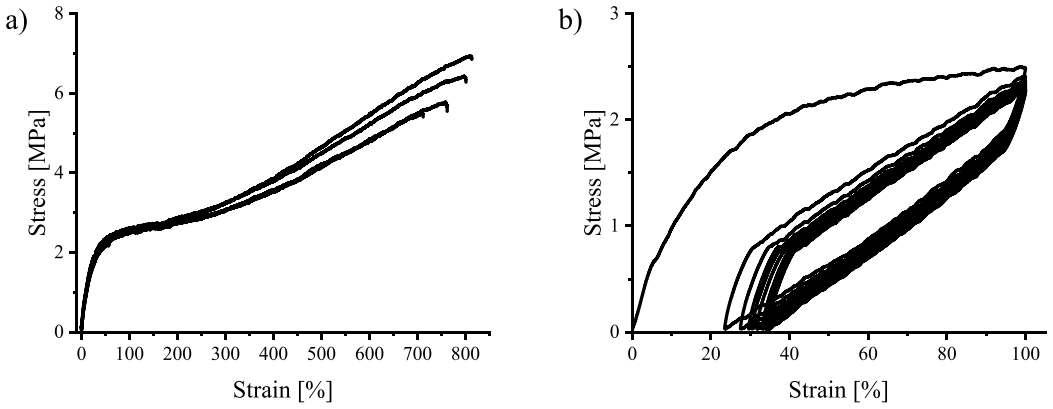

Figure 4. (a) Stress–strain curves of PE-b4.10/48. (b) Cyclic tensile test with a constant strain of 100%.

Synthesis and Properties of a Thermoplastic Elastomer. In order to demonstrate the versatility of polyesters derived from 2,3-BD, our objective was to produce thermoplastic elastomers (TPEs). Although the use of long chain aliphatic monomers in TPEs has been previously reported, they are typically used in combination with commercial polyethers such as PTMG or PPDO.[34,49] For our study, we selected PE-b4.10 as the soft segment due to its amorphous nature, while the very long chain monomer C_{48} was chosen as the hard segment.[34]

Therefore, a copolymer of dimethyl sebacate (C_{10} diester) and C_{48} diester in a molar ratio of 12:1 along with 2,3-BD was synthesized using the aforementioned process. This ratio of 12:1 corresponds to a theoretical average molecular weight of 3000 g mol^{-1} for the soft segment, and to 18 wt % of hard segment and 82 wt % of soft segment. The resulting polyester PE-b4.10/48 exhibited a molecular weight of 47,000 g mol^{-1} ($Đ$ = 1.8). The polymer displayed a complex melting profile, with the higher melting point at T_m = 76 °C (cf. Figure S29). Additionally, the injection molded specimens used for stress–strain measurements exhibited high transparency (cf. Figure S30).

Stress–strain measurements conducted on injection molded specimens demonstrated a characteristic behavior of elastic materials with a high ductility (E_t = 11 MPa, ε_{tb} = 772%). Cyclic tensile tests revealed a good recovery, with a residual strain of 34% (Figure 4).

Enzymatic Degradation. To assess the biodegradability of the branched polyesters, we conducted a preliminary enzymatic hydrolysis study of PE-b4.18 and the comparable linear polyester PE-4.18 using a pH-stat titration method, by which the numbers of ester bonds hydrolyzed over time are quantified by back-titration of OH^- upon liberation of H^+ during ester bond hydrolysis. Upon exposure of small melt pressed films to cutinase from the fungi *Humicola insolens* (HiC), both polyesters were hydrolyzed with linear rates for up to 2 weeks (Figure 5). At this time, PE-b4.18 and PE-4.18 reached hydrolysis extents of 63 (±6) % and 15 (±4) %, respectively, representing a 4-fold increase in enzyme-catalyzed hydrolysis rate for the branched polyester over the linear one. This difference in rate agrees well with current understandings of polyester biodegradability, with polyesters with lower thermal transitions and lower crystallinities being more amenable to enzyme-catalyzed hydrolysis.[50−52] In agreement with this trend, the higher-T_m PE-b4.26 did not show any hydrolysis upon exposure to HiC (cf. Figure S31) even at 40 °C.

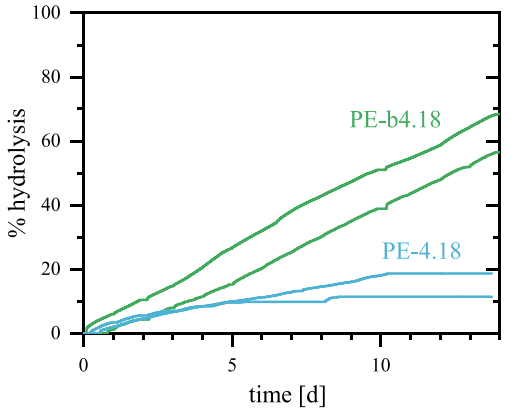

Figure 5. Enzymatic hydrolysis of films of PE-b4.18 and the linear analog PE-4.18 by *Humicola insolens* cutinase at 30 °C. See Figures S32–33 of the Supporting Information for additional data.

CONCLUSIONS

In conclusion, our study reveals the potential of utilizing 2,3-butanediol as a monomer for the production of semicrystalline polyesters in conjunction with long chain aliphatic dicarboxylate monomers. The challenges associated with the lower reactivity of the secondary alcohol 2,3-BD can be overcome, as demonstrated by the synthesis of high molecular weight polymers with up to M_n = 59,000 g mol^{-1} and M_w = 135,000 g mol^{-1} as determined by SEC vs polystyrene standards. The transition from an amorphous or molten polyester to a solid material occurs at a dicarboxylate chain length of C_{14} to C_{16}. As the monomer chain length increases, both the melting temperature and crystallinity of the polyesters increase. A pseudohexagonal structure was observed in polyesters with a dicarboxylate chain length up to C_{26}, while a polyethylene-like orthorhombic crystal structure was found in PE-b4.48. Tensile testing revealed a ductile behavior of the polyesters, with a Young's modulus of 290 MPa, yield strength of 10.8 MPa, and elongation at break of 430% for PE-b4.18.

Additionally, the synthesis of a thermoplastic elastomer, a copolymer of C_{10} diester, C_{48} diester, and 2,3-BD, further highlights the versatility and potential applications of polyesters derived from 2,3-BD. The resulting TPE exhibited high ductility and reasonable recovery properties.

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Observed enzyme-catalyzed hydrolysis of PE-b4.18 indicates potential biodegradability of branched, long-chain aliphatic polyesters, which is perhaps even enhanced over linear analogs. Further investigations into their degradation under environmental conditions are warranted.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07665.

Supplementary methods and data, including additional characterization of PE-b4.X (NMR spectra, GPC traces, DSC traces, WAXS measurements, and tensile testing) (PDF)

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Author Contributions

M.B. and H.S.M. performed syntheses and polymer analyses. T.F.N. carried out enzymatic degradation studies. M.B., T.F.N., and S.M. wrote the manuscript.

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Notes

The authors declare no competing financial interest.

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