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Erythritol Dicarbonate as Intermediate for Solvent- and Isocyanate-Free Tailoring of Bio-Based Polyhydroxyurethane Thermoplastics and Thermoplastic Elastomers

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Supporting Information

ABSTRACT: The highly reactive [4,4'-bi(1,3-dioxolane)]-2,2'-dione (BDC), also being referred to as erythritol dicarbonate and butadiene dicarbonate, enables the facile isocyanate-free tailoring and melt-processing of bio-based polyhydroxyurethane (PHU) materials. Both the direct carbonation of erythritol and the chemical fixation of CO₂ with 2,2'-bioxirane, obtained by epoxidation of bioethanolderived butadiene, afford high purity BDC in high yields. According to the FTIR spectroscopic model study BDC reacts with primary alkylamines at room temperature even in the absence of catalysts. High BDC reactivity is essential for



producing high molar mass linear PHU thermoplastics via melt-phase polyadditition with aliphatic diamines. Opposite to conventional isoycanate-mediated polyurethane syntheses erythritol units are incorporated into the polyurethane backbone without requiring the use of protective groups. As a function of the diamine structures and copolymer compositions the PHU properties vary from hard to soft and elastomeric. Typically isophorone diamine (IPDA) and trimethylhexamethylenediamine (TMHMDA) serve as building blocks for hard segments whereas highly flexible diamines such dimer fatty acid-derived diamidoamines render PHU soft and elastomeric. This study elucidates how copolymer composition and reaction parameters such as temperature, catalyst, and stabilizer addition influences PHU molar masses as well as mechanical and thermal properties. For the first time, owing to extraodinary BDC reactivity, melt-phase BDC polyaddition with diamines is competitive with conventional reactive processing of polyurethane thermoplastics using isocyanates. Moreover this versatile isocyanate-free synthetic route offers a great variety of options for fabricating unconventional bio-based PHUs and carbohydrate urethanes unparalleled by conventional polyurethanes.

INTRODUCTION

Tailored linear polyurethanes are melt-processable by extrusion and injection molding on heating, harden on cooling, and enable multiple thermal reprocessing steps without sacrificing their structural integrity. Albeit thermoplastic polyurethanes (TPU) represent only 5% of the total polyurethane consumption, they serve the needs of diversified markets ranging from engineering thermoplastics to thermoplastic elastomers. Typical TPU applications include textiles, footwear, tubes, sheets, films, protective coatings, and adhesives.^{1,2} Balancing of soft and hard segments in multiphase TPUs governs mechanical and thermal properties as well as solvent and wear resistance. Since several decades multiphase TPUs are fabricated by polyaddition of aromatic and aliphatic diisocyanates with short-chain diols such as butanediol together with flexible long-chain diols such as polyester or polyether diols, respectively.³⁻⁸ In 2013, BASF SE jointly with Adidas

engineered expanded multiphase TPUs (Infinergy) as shoe sole materials for "Energy Boost" running shoes by joining together the beneficial properties of TPUs and foams.⁹ Because of the resilience of tailored TPUs, the sole springs back into its original shape immediately after impact. Hence, this rebound effect enables efficient dampening and the runners use up considerably less energy. In view of sustainability and green chemistry, it is highly desirable to employ renewable resources and to substitute toxic and highly moisture sensitive isocyanate intermediates without impairing TPU melt processing. In traditional isocyanate-based polyurethane chemistry bio-based feedstocks are employed as alternative to substitute fossil resources in manufacturing of isocyanates and polyols. For

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example, the phosgenation of decarboxylated lysine yields pentamethylene diisocyanate as bio-based diisocyanate monomer.¹⁰ Since many years sugar polyols, prepared by propoxylation and ethoxylation of sugars, serve as polyol components of cross-linked polyurethanes.^{11–19} However, the incorporation of polyfunctional sugars into linear polyurethanes is much more difficult and requires the use of protective groups to render them difunctional.^{11,12} In view of green chemistry, high resource efficiency, and economy, the use of protective groups is prohibitive. During recent years considerable progress has been made regarding the development of non-isocyanate polyhydroxyurethanes, also being referred to as nonisocyanate polyurethane (NIPU), and prepared by polyaddition of polyfunctional cyclic carbonates with polyfunctional aliphatic amines.^{13–17} Owing to the rather low reactivity of most polyfunctional carbonates, readily available by carbonation of bio-based polyols or epoxidized terpenes and plant oils, respectively, the PHU synthesis requires the addition of catalysts such as triethylamine, organometallic complexes, diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and thiourea.¹⁸⁻²¹ Among them, TBD is emphasized for its high activity.^{22,23} Today even in the presence of catalysts PHU synthesis by solution polyaddition requires elevated temperatures and prolonged reaction times of several hours.^{11,12,14,24-28} According to Besse et al., long polymerization time accounts for massive side reactions which disrupt the precise stoichiometry, thus preventing molar mass buildup even in the presence of small amounts of monofunctional byproducts.^{3,13,14,29-31} It is an important challenge in TPU synthesis to enhance the polymerization rate of difunctional cyclic carbonates without impairing stoichiometry in order to produce high molar mass TPU within only a few minutes, typical for industrial reactive processing such as reactive injection molding and reactive extrusion. At Union Carbide Whelan et al. recognized first that [4,4'-bi(1,3-dioxolane)]-2,2'dione (BDC), also known as erythritol dicarbonate or butadiene dicarbonate, respectively, reacted with hexamethylenediamine (HMDA) in dimethyl sulfoxide solution at room temperature to yield linear PHU.³² However, they did not report on either reaction kinetics or basic structure/ property correlations. To the best of our knowledge, no attempts have been made to produce erythritol-based linear TPUs by solvent-free polyaddition and reactive melt processing. Erythritol, a common sweetener for diet food, is readily available by fermentation of bio-based feedstocks like glucose, sucrose, and other sugars.^{33–36} Carbonation by transesterification of meso-erythritol with dialkyl carbonates gave rather poor yields of impure erythritol dicarbonate which did not qualify as monomer for polyaddition without extensive purification. As reported by Rokicki et al., a monofunctional

cyclic ether carbonate is formed as byproduct (see Scheme 1).^{32,37–39} The presence of small amounts of such monofunctional cyclic carbonates drastically impairs PHU molar mass.

Herein we report on the synthesis of high purity BDC from *meso*-erythritol by transesterification with diphenyl carbonate without encountering monofunctional cyclic carbonate as undesirable byproduct (see Scheme 1, route A). In a highly atom-efficient alternative synthetic pathway BDC is obtained without byproducts by epoxidation of butadiene followed by chemical CO₂ fixation (see Scheme 1, pathway B).³⁷ Bio-based butadiene can be gained from bioethanol.⁴⁰ We examine the influences of amine structures, catalyst, and stabilizer addition on PHU formation (see Scheme 2) in order to enhance polymerization rate without encountering side-reactions in melt-phase polyaddition.





This study elucidates how the choice of diamine structures, particularly blending together rigid diamines with flexible diamines such as dimer fatty acid-based diamidoamines, governs thermal and mechanical properties of bio-based PHU thermoplastics and thermoplastic PHU elastomers.

EXPERIMENTAL SECTION

Chemicals. DMSO (99%) and ethylene carbonate (EC, 99%) were obtained from Merck, THF (99%) was from Carl Roth, tetrabutyl-ammonium bromide (TBAB, 99%) and hexamethylenediamine (HMDA) were from Alfa Aesar GmbH & Co. KG. Carbon dioxide (N45) was obtained from Air Liquide. All deuterated solvents were purchased from Deutero GmbH. The dimer fatty acid Pripol 1009 was supplied by Croda GmbH and acetic anhydride (99%) by Fluka Analytical. The diamines such as 2,2,4-trimethylhexamethylenediamine (TMHMDA), isophoronediamine (IPDA), triethyl orthoformiate (99%), DABCO, ethanol (99%), *meso*-erythritol (99%), 1,8-diaminooctane (OCDA), and 1,12-diaminododecane (DDA) were purchased from Sigma-Aldrich Chemie GmbH. Irgafos 168 and Irganox 1010 were supplied by BASF SE.

Scheme 3. BDC Preparation from 2,2'-Dioxirane and meso-Erythritol



FT-IR Spectroscopy. Fourier transform infrared spectra were measured on a Vector 22 from Bruker. The attenuated total reflection measurements were recorded by using 30 scans between 4000 and 800 cm⁻¹.

Thermogravimetric Analysis. Simultaneous thermal analysis (STA 409 from Netzsch) was used to study the degradation and the mass loss in an air atmosphere using a temperature range varying between 50 and 650 $^{\circ}$ C at 10 K/min.

NMR Spectroscopy. NMR spectroscopy measurements were recorded at a frequency of 300 MHz using the Avance II spectrometer from Bruker. Acetone- d_6 , CDCl₃, and DMSO- d_6 were used as deuterated solvents.

Differential Scanning Calorimetry. A DSC-1 PerkinElmer and a Netzsch DSC 204 F1 Phoenix (heating rate 10 or 20 K/min) were used to determine the thermal properties.

Stress–Strain Characterization. Zwick Z005 (Ulm, Germany, ISO527A1, 50 mm/min) was used to characterize the mechanical properties of injection-molded dog bone-shaped testing specimen. Elongation at break and Young's modulus and were determined at room temperature by using the statistical average of at least five testing samples.

Size Exclusion Chromatography. The molar mass was determined using THF and DMAc solution by means of a SECurity GPC-System (Agilent 1200) from PSS Polymer Standards Service GmbH. Three SEC columns with pore size of $(10^2, 10^{-3}, and 10^{-4} \text{ Å}$ for THF and 30 and 1000 Å for DMAc) from PSS Polymer Standards Service GmbH were used in order fractionate the polymer samples using the refractive index detector G136A and VW-detector G1314B from Agilent Technologies. Polystyrene was used as standard for samples in THF and PMMA for polymers measured in DMAc at 85 °C. All PHU samples were acetylated with acetic anhydride prior to the SEC measurement.

Compounder. The reactive compounding was made using a Micro $5 \text{ cm}^3/15 \text{ cm}^3$ twin-screw compounder from Xplore in a temperature range between 70 and 140 °C. The speed of the twin screw was kept constantly at 120 rpm. The gained force-time and temperature-time diagrams were recorded by using DSM Xplore as software.

Synthesis of BDC from 2,2'-Bioxirane. Tetrabutylammonium bromide (TBAB, 0.96 mmol, 312 mg, 0.50 mol %) was added to an autoclave which was flushed with CO₂. Under a CO₂ atmosphere 2,2'-dioxirane (15 mL, 16.7 g, 0.194 mol) was added. The carbonation took place at 30 bar and 120 °C for the duration of 6 h. The solid product was recrystallized from acetone and dried overnight in a vacuum. BDC was obtained as a colorless powder (90%) melting at 169 °C (lit.: 90%, $T_{\rm m}$ 166 °C).³⁷ ¹H NMR (299.87 MHz, acetone- d_6): δ = 4.38–4.47 (m, 2 H, 1–CH₂), 4.60–4.70 (t, 8.8 Hz, 2 H, CH₂), 5.04–5.13 (m, 2 H, CH) ppm.

BDC from *meso*-Erythritol. Diphenyl carbonate (DPC, 92.1 g; 0.43 mol; 2.10 equiv), Zn(OAc)₂·2H₂O (451.1 mg; 1 mol %), DMSO (45 mL, 4.5 mol/L), and *meso*-erythritol (25 g, 0.21 mol) were added to a flask. This mixture was heated at 30 mbar to 120 °C and stirred for 19 h. During the conversion DMSO and phenol were distilled off, and the residual brown solid was recrystallized from acetone. BDC was gained as a colorless crystalline product (80–90%) with a melting point of 169 °C (lit.: 168–170 °C)^{39,41} which has a purity of 99% (determined by NMR spectroscopy). ¹H NMR (299.87 MHz, DMSO- d_6): $\delta = 4.35-4.45$ (*m*, 2 H, CH₂), 4.58–4.68 (*m*, 2 H, CH₂), 5.12–

5.20 (*m*, 2 H, CH₂) ppm. ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 65.19$ (2 C, CH₂), 75.93 (2 C, CH₂), 154.63 (2 C, C=O) ppm.

Dimer Fatty Acid-Based Diamidoamine (DFS-1,6-AA). Pripol 1009 (250 g, 0.441 mol) was mixed with triethyl orthoformiate (146 mL, 131 g, 0.887 mol, 2.10 equiv) and EtOH (240 mL), and few drops of sulfuric acid were added. The mixture was refluxed for 240 h. All byproducts were distilled off in a vacuum. The remaining viscose mixture was dissolved in Et₂O and extracted with H₂O (3 × 200 mL). Organic phases were dried first over MgSO₄ and afterward overnight in a vacuum at 60 °C. ¹H NMR (299.87 MHz; CDCl₃): δ = 0.70–1.77 (m, 67.80 1-H, CH₂), 2.27 (t, 4.17 3-H, CH₂), 4.11 (q, 4.0 2-H, CH₂) ppm.

The resulting dimer fatty acid diethyl ester (95.9 g, 154 mmol) was mixed with HMDA (251 g, 2.17 mol, 14.0 equiv) for 170 h at 115 °C. After complete conversion excessive HMDA was distilled off. The residual viscose oil was dissolved in Et₂O (300 mL) and extracted with water (5 × 500 mL). All organic phases were combined and dried at 60 °C in a vacuum for 24 h. DFS-1,6-AA ($n(\text{Amin}) = 2.33 \pm 0.20$ mol/kg) was gained as a viscose brown oil. A dimer content of 14.3 mol % was determined by ¹H NMR spectroscopy. ¹H NMR (299.87 MHz; CDCl₃): $\delta = 0.23-1.92$ (m, 74.46 2-H, CH₂), 2.08 (t, 4.24 4-H, CH₂), 2.61 (t, 4.24 1-H, CH₂), 3.16 (q, 4.00 3-H, CH₂) ppm.

General Procedure for PHU Preparation in DMSO Solution. The aliphatic diamine (HMDA, OCDA, DDA) was dissolved in DMSO (1 mol/L) at 100 °C. An exact equivalent of BDC was added to this mixture. After 14–20 h of stirring at 100 °C the reaction was cooled down to room temperature. By addition of water the polymer was precipitated as a colorless solid. The product was dried at 60 °C in a vacuum.

BDC_HMDA. ¹H NMR (299.87 MHz; DMSO- d_6): $\delta = 1.1-1.5$ (*m*, CH₂), 2.8–3.1 (*m*, CH₂), 3.4–3.9 (m, CH–OH), 4.0–4.3 (*m*, O=C–CH₂ 4.5–4.7 (*m*, O=C–CH) 4.9–5.1 (*m*, OH), 6.6–7.2 (*m*, NH) ppm.

BDC_OCDA. ¹H NMR (299.87 MHz; DMSO- d_6): $\delta = 1.1-1.5$ (*m*; CH₂), 2.8–3.1 (*m*, CH₂), 3.5–3.9 (*m*, CH–OH), 4.0–4.7 (*m*, O=CH, O=C-CH₂), 4.8–5.1 (*m*, OH), 6.6–7.2 (*m*, NH) ppm.

BDC_DDA. ¹H NMR (299.87 MHz; DMSO- d_6): $\delta = 1.2-1.7$ (*m*, CH₂), 2.9-3.2 (*m*, CH₂, 1/1'), 3.5-4.0 (*m*, CH-OH), 4.0-4.7 (*m*, O=CH, O=C-CH₂), 4.9-5.2 (*m*, OH), 6.7-7.2 (*m* NH) ppm.

General Procedure for Melt-Phase Polyaddition of BDC with Diamines. *Kinetic Study*. DFS-1,6-AA was warmed to 70 °C and mixed with the exact stoichiometric amount of BDC and the additive, e.g. DABCO, Irgafos168, or the blend 50 wt % Irganox1010/50 wt % Irgaphos168, (0.5 wt %) for 1 min. The viscous mixture was injected into the compounder (Micro 5 cm³/15 cm³ twin-screw compounder/Xplore), which was set at 80 °C. The polymer buildup was monitored for 85 min, every 10 min a sample was taken. To avoid polymer degradation by shear forces torque was kept almost below 3000 N. When achieving this force value, the temperature was increased to 100 °C.

General Preparation of Homo- and Copolymers. The mixture of catalyst (0.5 wt %), stabilizer (0.5 wt %), and the diamines was warmed up to 70 °C. Then the exact stoichiometric amount of BDC was added, and the mixture was stirred for few minutes. The viscous reaction mixture was injected into the compounder (Micro 5 cm³/15 cm³ twin-screw compounder/Xplore) and processed at 80 °C until the force increased at a maximum torque of 3000 N. In such case the temperature was then increased in 20 °C intervals up to 130 °C. Increasing molecular weight of the resulting polymers is accompanied



Figure 1. FTIR spectroscopic analyses of reaction kinetics monitoring the reaction of EC, BDC (O=C: 1800 cm⁻¹) with ethanolamine at room temperature in the absence of solvent at 1, 15, and 32 min for BDC and at 1, 60, and 120 min for EC yielding urethane (O=C: 1700 cm⁻¹).

Scheme 4. Solution Polyaddition of BDC with 1,6-Hexamthelenediamine (HMDA, x = 6), 1,8-Octamethylenediamine (OCDA, x = 8), and 1,12-Dodecanediamine (DDA, x = 12) in DMSO (1 mol/L) at 100 °C



by higher melt viscosity and increased shear forces. DFS-1,6-AA and the used additive (0.5 wt %) were mixed at 70 °C for several minutes. After exactly 20 min the prepared polymer was injected at 130 °C and 9 bar into the mold to give dog-bone-shaped testing specimens. To prevent side reactions, the conversion temperature was always kept below 140 °C.

RESULTS AND DISCUSSION

BDC Preparation. As is illustrated in Schemes 1 and 3, the carbonation of both meso-erythritol and 2,2'-bioxirane affords BDC. As compared to conventional transesterification of mesoerythritol with dimethyl carbonate, accompanied by monofunctional carbonate byproduct formation, both BDC yield and purity significantly improved when meso-erythritol was transesterified with diphenyl carbonate (DPC) in DMSO solution at 120 °C in the presence of zinc acetate as catalyst.^{37–39} During this transesterification reaction DMSO together with phenol, which evolved as byproduct, were continuously removed by vacuum distillation. In sharp contrast, the carbonation of 2,2'dioxirane (BDO), readily available by epoxidation of butadiene, proceeded at 120 °C and 30 bar CO₂ pressure in the presence of tetrabutylammonium bromide (TBAB) as catalyst without requiring either solvent addition or removal of byproducts. Hence, this bulk carbonation represents an atom-efficient route to BDC. As confirmed by means of ESI, NMR, and FTIR spectroscopy (see Supporting Information) both routes afford high purity BDC melting at 169 °C and containing 55.5 wt % chemically fixed CO₂.

Model Reactions of BDC with Amines. The accelerating effect of vicinal cyclic carbonate groups was already predicted by Goldstein et al., who investigated the aminolysis kinetics of carbohydrate-based cyclic carbonates in DMSO.⁴² The high reactivity of BDC was recognized first by Whelan et al., who

disclosed that BDC reacted with primary alkylamines in DMSO solvent at ambient temperature.³⁷ In order to examine BDC conversion at room temperature in the absence of solvents, the reactions of both BDC and the corresponding monofunctional ethylene carbonate with ethanolamine were monitored by means of FTIR spectroscopy using identical reaction conditions. In the FTIR traces (see Figure 1) of the BDC/ ethanolamine reaction the IR band at 1800 cm⁻¹ corresponds to the stretching vibration of the carbonyl group of the cyclic carbonate while the signal at 1700 cm⁻¹ represents the carbonyl group of the formed PHU urethane bond. Full BDC conversion with ethanolamine was achieved at room temperature within 32 min.

In sharp contrast, the corresponding bulk reaction of the much less reactive ethylene carbonate with ethanolamine was significantly slower, requiring 120 min for achieving full conversion. This confirms that the inductive effect of the vicinal carbonate group renders BDC significantly more reactive. This is in accordance with a similar substituent effect observed for sorbitol tricarbonate.⁴³

Linear PHUs Prepared by Solution Polyaddition. Albeit BDC is known for several years only Whelan et al. reported on BDC polyaddition with diamines in DMSO to produce linear PHUs at ambient temperature.³² However, they did not comment either on polymerization kinetics, molecular PHU architectures, or PHU material properties. Therefore, we investigated DMSO solution polyaddition of BDC with 1,6hexamethylenediamine (HMDA), 1,8-octamethylenediamine (OCDA), and 1,12-dodecamethylenediamine (DDA) in DMSO (1 mol/L) at 100 °C, following procedures reported by Kihara et al. for the preparation of other linear PHUs.⁴⁴ Scheme 4 displays the reaction pathways leading to PHU isomers containing either secondary hydroxyl groups or



Figure 2. ¹H NMR spectrum (DMSO- d_6) of PHU isomers (BDC_HMDA, x = 4) prepared by polyaddition in DMSO solution (1 mol/L) at 100 °C.

Table 1. Molar Mass and Thermal Properties of PHUs Prepared by Solution Polyaddition of BDC with HMDA, OCDA, or DDA in DMSO at 100 $^{\circ}C^{a}$

polymer	$M_{n,NMR}^{b} [g/mol]$	$M_{n,SEC}$ [g/mol]	$M_{\rm w}^{\ c} \left[{\rm g/mol} \right]$	PDI ^b	\mathbb{P}^{d} [%]	$T_{g} [^{\circ}C]$	$T_{\rm m} [^{\circ}C]$	(prim OH/sec OH) ^{b,e} [%]
BDC-HMDA	14800	9700	23100	2.4	98	9		34/66
BDC-OCDA	8900	9600	26900	2.8	97	9		35/65
BDC-DDA		10000	31300	3.1	98	11	141	

^{*a*}Solution polyaddition (DMSO; 1 mol/L) 14–19 h at 100 °C. ^{*b*}Determined by ¹H NMR spectroscopy. ^{*c*}SEC of acetylated PHUs in DMAc, solution using a PMMA standard, 85 °C; DSC 10 K/min. ^{*d*}Conversion (*P*) as determined by ¹H NMR spectroscopy. ^{*e*}Molar ratio (OH) of primary (Prim) and secondary (Sec) hydroxyl groups as determined by ¹H NMR spectroscopy.

primary hydroxyl groups together with secondary hydroxyl groups in the backbone. This PHU isomer formation is accounted for by different ring-opening pathways following the attack of the amine at the carbonyl group.

The progress of the polyaddition was monitored by means of FTIR spectroscopy which confirmed full BDC conversion and successful urethane formation. All polymers were precipitated in water, washed with water, and dried in a vacuum at 60 °C for 24 h. The polymer structure was characterized by ¹H NMR spectroscopy. Figure 2 displays the ¹H NMR spectrum of the BDC-HMDA polymer. The hydrogen atoms allocated in the aliphatic chain segment, marked as (2), correspond to the two ¹H NMR signals at 1.15 and 1.50 ppm, whereas the aliphatic methylene hydrogen atoms next to the urethane group, marked as (1) and (3), are assigned to the broad signal at 2.90 ppm. Primary and secondary hydroxyl groups, labeled (5) and (5^*) , correspond to the two multiplet signals at 3.85 and 3.53 ppm (see Figure 2). The ratio between the primary and secondary OH groups of (35/65) was also determined by ¹H NMR spectroscopy. The formation secondary hydroxyl groups indicates that the ring-opening occurred by thermodynamic control. This is in accordance with other reports on the preparation of linear PHUs via polyaddition of cyclic carbonates and diamines.^{18,45} The hydrogen atoms labeled (4) and (5) of the methylene groups allocated in the α -position of the urethane oxygen atom account for broad signals at 4.50

and 4.70 ppm. The PHU molar masses determined by means size exclusion chromatography (SEC) using PHU solutions in DMAc and by ¹H NMR spectroscopic end-group analysis are listed in Table 1. The degree of polymerization was determined from the signal intensity ratio of ¹H NMR signals corresponding to the remaining amino group (2.65 ppm) at the PHU chain end and the methylene group (3.0 ppm) allocated next to the urethane in the PHU backbone. Independent of the diamine type, the molar ratio of primary and secondary hydroxyl groups was around 0.5. Preferably, erythritol 1,2-diol units are incorporated in the PHU backbone. Owing to the extremely low PHU solubility in THF, CHCl₃, or DMAc, hydroxyl and amine groups were acetylated with acetic anhydride prior to SEC analysis in order to enhance PHU solubility. It should be noted that this postpolymerization functionalization markedly increased PHU molar mass. Regardless of the diamine type and postpolymerization functionalization all PHU molar masses (M_w) were quite low and varied between 20 and 30 kg/mol. This is in accordance with observations by Whelan et al. for BDC-based NIPU and also with those of Kihara et al., who prepared other PHUs using the identical solution process conditions.^{32,44} Such low PHU molar masses do not qualify for industrial applications. Most likely owing to low PHU molar masses the type of diamine had little influence on glass transition temperatures ranging between 9 and 11 °C. In thermal analyses by DSC (see Table 1) only

BDC–DDA was semicrystalline and exhibited a melting temperature of 141 $^\circ \text{C}.$

Linear PHUs Prepared by Melt-Phase Polyaddition. Short polymerization times and fast molar mass buildup are essential for a reasonable technical process since side reactions, high viscosity, and crystallization restrict diffusion and lower reactivity of the end groups. Moreover, in order to qualify for reactive injection molding and reactive extrusion successfully competing with the exceptionally rapid polyaddition reaction of isocyanates, the polyaddition reaction of the cyclic carbonates should take place within minutes. To date, unlike BDC, most conventional difunctional cyclic carbonates even in the presence of catalysts exhibit poor reactivity and fail to produce linear PHUs by melt-phase polyaddition and reactive compounding within a few minutes. As is illustrated in Scheme 5, in order to tailor linear PHU thermoplastics and thermo-

Scheme 5. PHU Building Blocks Comprising Rigid Diamines (IPDA, TMHMDA, HMDA, DDA) and Flexible Dimer Fatty Acid-Based Diamidoamines (DFS-1,6-AA)



plastic elastomers by balancing hard and soft segments, BDC was polymerized with rigid diamines such as HMDA, DDA, 2,2-dimethyl-4-methylhexamethylenediamine (TMHMDA), and isophoronediamine (IPDA) in conjunction with flexible dimer fatty acid-based diamidoamines (DFS-1,6-AA) obtained by end-capping dimer fatty acid with HMDA.

The melt-phase polyaddition of BDC with diamine was performed using a twin-screw miniextruder (Micro 5 cm³/15 cm³ twin-screw compounder, XPLORE). It should be noted that the polymerization temperature of BDC polyaddition in melt phase is restricted to temperatures below 140 °C. Above 140 °C BDC alkylation, accompanied by evolution of carbon dioxide, competes with urethane formation and accounts for foaming and severely impairing stoichiometry required to afford high molar masses. In order to examine the influence of catalysts and antioxidants, BDC was polymerized with the flexible dimer-amidoamine DFS-1,6-AA in the presence of additives such as DABCO catalyst, phosphite processing stabilizer (Irgafos168), phenolic antioxidant (Irganox1010), and the corresponding stabilizer blend (50 wt % Irganox1010/ 50 wt % Irgaphos168). Typically, DFS-1,6-AA, BDC, and the additive such as DABCO, Irgafos168, and the blend of 50 wt % Irganox1010/50 wt % Irgaphos168 (0.5 wt %) were premixed at 70 °C for 1 min and then injected into the compounder at 80 °C. Owing to the rapid increase of viscosity, the temperature was increased to 100 °C and kept constant until the end of the experiment. Samples were collected after 15, 35, 55, 75, and 85 min. At low temperature the increase of molar mass was comparable in the presence and in the absence additives. Upon heating to 100 °C, the addition of catalyst and especially the addition of antioxidant markedly increased weight-average molar mass, as determined by SEC measurements (see Figure 3). Most likely, the antioxidant prevented oxidation of the



Figure 3. Weight-average molar mass (M_w) of BDC-DFS-1,6-AA as a function of polymerization time in the absence (left) and the presence of 0.5 wt % additives such as DABCO, Irganox1010/Irgafos168 (50 wt %/ 50 wt %) and Irgafos168. BDC was polymerized with stoichiometric amounts of DFS-1,6-AA for 40 min at 80 °C and 50 min at 100 °C.

amino groups during this reaction which impaired stoichiometry and thus lowered molar mass. From the torque measurements it became apparent that the molar mass increase occurred within 20 min at 100 $^{\circ}$ C in the presence of antioxidant and catalyst.

For the evaluation of the thermal and mechanical properties of BDC homo- and copolymers stoichiometric amounts of BDC and diamines were premixed together with 0.5 wt % TBD catalyst and 0.5 wt % Irganox1010/Irgafos168 (50 wt %/ 50 wt %) at 70 °C for 2 min and injected into the mini-twin-screw extruder (Xplore). After melt-processing for 20 min at 80-130 °C the samples were recovered and injection-molded at 135 °C. In order to balance soft and hard segments, 4, 10, and 20 wt % of the flexible DFS-1,6-AA was substituted by rigid diamines such as IPDA or TMHMDA, respectively. All samples were characterized by FTIR and NMR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). In order to improve their solubility all homo- and copolymers were acetylated with acetic anhydride prior to SEC analysis. Molar masses, molar mass distributions, and thermal and mechanical properties are summarized in Table 2. All BDC homo- and copolymers were melt-processable by injection molding. The copolymerization of BDC with flexible DFS-1,6-AA afforded a highly flexible soft PHU exhibiting low glass transition temperature of -5 °C and low Young's modulus of 90 MPa in conjunction with a high elongation at break of 130%. The stiffness of the BDC copolymers gradually increased with increasing content of rigid comonomers such as IPDA or TMHMDA, respectively. On increasing the rigid diamine content to 20 wt % the Young's modulus increased from 90 to 1470 MPa (+1600%) for DFS-1,6-AA/IPDA copolymers and to 980 MPa (+1200%) for DFS-1,6-AA/TMHMDA copolymers. The glass transition temperatures increased from -5 to 24 °C for IPDA- and 27 °C for TMHMDA-copolymers. As compared to IPDA copolymers, the TMHDMA copolymerization afforded markedly higher molar masses of the copolymer. This could be attributed to the higher reactivity of the TMHDMA amine groups with respect to IPDA. Moreover, the higher rigidity of IPDA, as evidenced by the higher glass transition temperature of the homopolymer, would require higher processing temperatures which are not feasible due to

Table 2. Molar Mass and Ther	nal Properties of BDC Homo- a	and Copolymers Prepared	l by Melt-Compounding fo	or 20 min at
80–130 °C	-			

polymer	IPDA or TMHMDA [wt %]	IPDA or TMHMDA [mol %]	T ^a [°℃]	$T_{\rm m}^{\ a}$ [°C]	$M_{\rm n}$ [g/mol]	$M_{ m w}$ [g/mol]	Young's modulus ^d [MPa]	elongation at break ^d [%]
BDC/DFS-1,6-AA	0	0	-5	133	9000 ^b	26200 ^b	90 ± 20	130 ± 40
BDC/DFS-1,6-AA/IPDA_1	4	20	-5	133	5900 ^b	20600 ^b	80 ± 30	120 ± 30
BDC/DFS-1,6-AA_IPDA_2	10	40	-3	111	6100 ^b	18800 ^b	300 ± 40	40 ± 40
BDC/DFS-1,6-AA_IPDA_3	21	60	24		5900 ^b	14800 ^b	1470 ± 140	<1
BDC/IPDA	100	100	88		2200 ^b	4700 ^b		
BDC/DFS-1,6-AA/TMHMDA_1	4	20	13		10000 ^c	42000 ^c	40 ± 10	220 ± 20
BDC/DFS-1,6-AA/TMHMDA_2	9	40	16		9600 ^c	44100 ^c	380 ± 70	<1
BDC/DFS-1,6-AA/TMHMDA_3	20	60	27		8500 ^c	33600 ^c	980 ± 50	<1
BDC/TMHMDA	100	100	41		12400 ^b	30800 ^b		
^a DSC: 10 K/min. ^b SEC (THF, PS standard). ^c SEC (DMAc, PMMA standard, 85 °C). ^d Tensile testing: ISO 527A1.								

side reactions. It should be noted that both BDC/IPDA ($T_g = 88 \text{ °C}$) and BDC/TMHDMA ($T_g = 41 \text{ °C}$) homopolymers were extremely brittle.

According to DSC analyses, only the BDC/DFS-1,6-AA homopolymers and BDC copolymers with DFS-1,6-AA/IPDA containing less than 40 mol % of IPDA incorporation were semicrystalline with melting temperatures varying between 111 and 131 °C. Opposite to IPDA the branched TMHMDA prevents crystallization during injection molding. This may be attributed to the stereochemistry of the branched segments in the PHU backbone. In addition for all polymers any by product formation could be detected by ¹H NMR spectroscopy.

CONCLUSIONS

The carbonation of both erythritol and epoxidized butadiene affords high-purity bio-based [4,4'-bi(1,3-dioxolane)]-2,2'dione (BDC) as versatile and highly reactive difunctional cyclic carbonate intermediate enabling the solvent-free fabrication of unconventional linear non-isocyanate carbohydrate-urethane thermoplastics unparalleled by classical polyurethanes. Since isocyanates readily react with all hydroxyl groups, conventional polyaddition of erythritol with diisocyanates forms cross-linked polyurethanes. Hence, protective groups are needed to convert erythritol into a diol useful as mononmer in conventional isocyanate-based synthesis of poly(carbohydrate-urethane)s. Whereas the known erythritol carbonation with dimethyl carbonate yields BDC together with considerable amounts of monofunctional cyclic carbonate impurities, the transesterification of erythritol with diphenyl carbonates substantially improves both BDC yield and purity. Neither solvent nor byproduct removal is required when 2,2'-bioxirane, obtained by epoxidation of bioethanol-derived butadiene, is converted into BDC by means of catalytic CO₂ fixation. According to FTIR monitoring of the BDC reaction with amines full BDC conversion and quantitative urethane formation is achieved at ambient temperature within a few minutes. This remarkably high BDC reactivity is by far superior to most other difunctional cyclic carbonates. Hence, for the first time BDC enables the rapid melt-phase polyaddition with various aliphatic diamines to form high molar mass linear PHU thermoplastics by reactive processing. In sharp contrast, most state-of-the-art syntheses of linear PHU thermoplastics require solution polymerization and polymerization times of several hours. It should be noted that the polymerization temperature is restricted to temperatures below 150 °C, owing to alkylation side reactions occurring at higher temperatures. The addition of catalysts and especially antioxidants such as sterically hindered

phenols during melt-phase polymerization prevents side reactions which impair stoichiometry and PHU molar masses. The melt-phase polyaddition of TMHMDA with BDC affords linear PHU with weight-average molar mass of 44 kg/mol within 20 min at 100 °C. This solvent-free polyaddition is superior to conventional BDC solution polymerizations requiring reaction times of several hours and producing PHUs with much lower molar masses. Especially in the presence of flexible dimer fatty acid-derived diamidoamine all resulting BDC copolymers are melt processable by meas of injection-molding. Combining flexible and rigid diamines governs the formation of segmented PHU thermoplastics with properties varying from hard to semicrystalline, amorphous, flexible, and soft. Progress in BDC-mediated melt-phase polyaddition holds great promise for the isocyanate-free formation of polyurethane thermoplastics, thermoplastic elastomers, and specialty polymers by reactive extrusion and reactive injection-molding.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b02787.

SEC, thermic, and mechanic analysis of all materials as also as the FTIR and ¹H NMR spectra; force-time and temperature-time diagrams (PDF)

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Notes

The authors declare no competing financial interest.

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