Macromolecules

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Isocyanate-Free Route to Poly(carbohydrate−urethane) Thermosets and 100% Bio-Based Coatings Derived from Glycerol Feedstock

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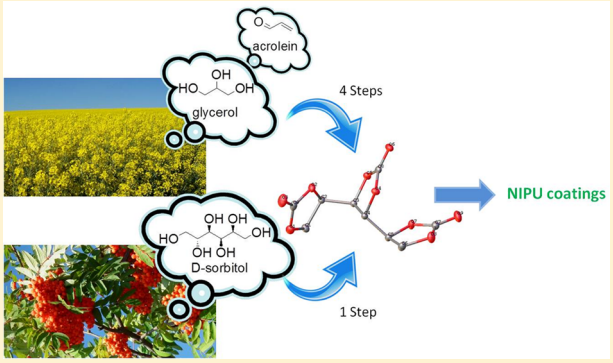
Supporting Information

ABSTRACT: Glycerol serves as the exclusive bio feedstock for the preparation of high purity sorbitol tricarbonate (STC) as new intermediate for poly(carbohydrate−urethane) thermosets and 100% bio-based non-isocyanate polyhydroxyurethane (NIPU) coatings. In this process, glycerol-based acrolein is dimerized, carbonated, and oxidized, thus producing the highly reactive diepoxy functional ethylene carbonate (DOC), which by facile chemical CO_2 fixation yields high purity STC. Opposite to most state-of-the-art multifunctional five-membered cyclic carbonates and regardless of the feedstock used for its manufacture, STC enables amine curing at ambient temperature even in the absence of catalysts. According to FT-IR and NMR spectroscopic analyses of the amine/carbonate reaction kinetics, the internal cyclic carbonate group is 3 times more reactive with respect to the two terminal carbonate groups. This is attributed to the electron-withdrawing effect of terminal cyclic carbonates. Curing STC with a blend of bio-based flexible and rigid diamines such as dimer fatty acid-based diamine (Priamine 1074) and isophorone diamine affords poly(carbohydrate−urethane) thermosets and NIPU coatings exhibiting substantially improved thermal and mechanical properties.



INTRODUCTION

Today most poly(carbohydrate−urethane) and poly(carbohydrate−ester−urethane) polymers are produced by curing saccharide-based polyols with isocyanates.[1−4] For industrial use it is highly attractive to exploit bioresources such as glycerol, which is an abundant side product of biodiesel production.[5−10] The two largest suppliers of glycerol in the world are Germany and Malaysia.[11] Currently, glycerol is employed as bio-based feedstock for manufacturing of polyglycerol, acrylic acid, acrolein, epichlorohydrin, and glycidol.[12] Acrolein, available by dehydration of glycerol and other routes, is produced worldwide in 350 kt/a scale.[13] Besides acrylic acid production, one of the most important industrial application for acrolein is its conversion into DL-methionine, an amino acid which is essential for animal growth and employed as animal food additive in meat production.[14] Applications of glycerol in polymer synthesis span from the production of polyglycerol to epichlorohydrin, e.g., in Solvay's Epicerol process, which is industrially exploited as intermediate for producing epoxy resins.[15] Hence, bio-based epichlorohydrin is employed to convert biopolyols such as glycerol and saccharides into bio-based epoxy resins, which on carbonatization by chemical fixation of carbon dioxide affords multifunctional cyclic carbonates as intermediates for non-isocyanate polyhydroxyurethanes (NIPU).[16] The formation of NIPU from glycidyl ethers is illustrated in Scheme 1. Unlike conventional polyurethane production, NIPU synthesis does not require toxic intermediates such as phosgene and highly moisture sensitive isocyanates. However, in sharp contrast to isocyanates, most cyclic carbonates are considerably less reactive and require amine cure at elevated temperatures and catalyst addition.[17−19]

Fleischer et al. reported on bio-based NIPUs derived from glycidyl ethers of pentaerythritol (PEC) and trimethylolpropane (TMC).[8] An overview on cyclic carbonate and NIPU syntheses including the use of glycerol and saccharide feedstocks was given by Blattmann and Mülhaupt.[20] Sorbitol tricarbonate is known since the 1960s, but it has not yet been exploited as intermediate in NIPU synthesis.[21] Most likely, this is attributed to difficulties encountered in the direct carbonatization of saccharides and its tedious purification.[22] Such synthetic problems are also well-known for the esterification of saccharides such as sorbitol, yielding complex reaction mixtures.[22−27] Moreover, unlike saccharide−glycidyl ether-based cyclic carbonates, which are

Received: July 12, 2016
Revised: September 20, 2016

DOI: 10.1021/acs.macromol.6b01485
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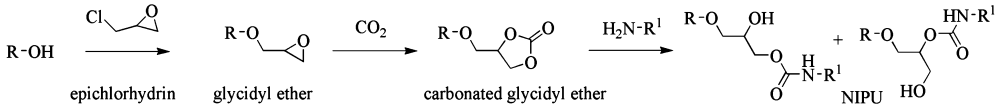
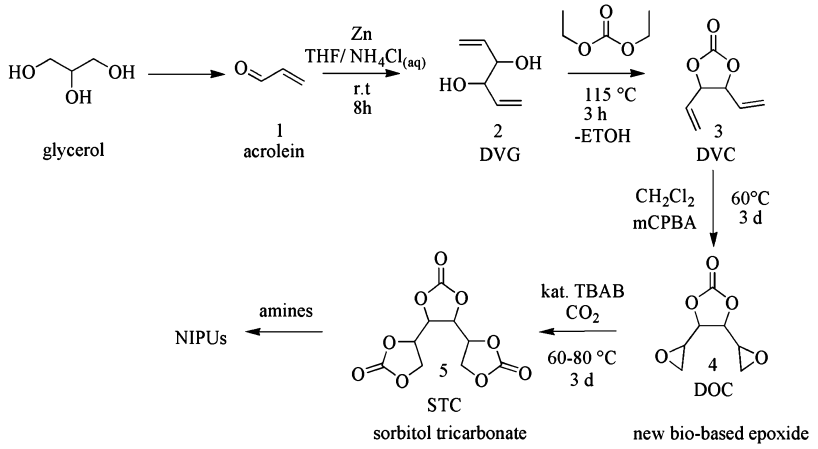
Scheme 1. Synthesis of Conventional Cyclic Carbonates Derived from Glycidyl Ethers by Chemical Fixation of CO_2 and Its Conversion with Amines to NIPU



Scheme 2. Preparation of Sorbitol Tricarbonate (STC) Derived from Glycerol Feedstock



viscous liquids and easy to handle in NIPU synthesis, the pure sorbitol tricarbonate is a crystalline solid, melts at high temperature of 230 °C close to its decomposition, has low solubility in nonpolar media, and is highly immiscible with most NIPU components.[21,28,29]

Here, we present synthetic strategies for preparing high purity sorbitol tricarbonate and for tailoring novel poly(carbohydrate−urethane) thermosets derived from glycerol feedstock. As illustrated in Scheme 2, acrolein (**1**), which is industrially available by the dehydration of glycerol, was dimerized by means of the zinc-catalyzed McMurry coupling reaction to produce divinyl ethylene glycol (DVG, **2**). Then DVG was converted into divinyl ethylene carbonate (DVC, **3**) by transesterfication with diethyl carbonate following procedures reported by Trost et al.[30,31] Finally, the two terminal carbonate groups were introduced via epoxy-mediated CO_2 conversion with the highly reactive diepoxy carbonate (DOC, 4,5-diepoxy-2-yl-1,3-dioxolan-2-on, 4), readily available by DVC oxidation. Alternatively, STC is also available by conversion of sorbitol with diphenyl carbonate (see Supporting Information). Sorbitol tricarbonate (STC, **5**) and its corresponding liquid prepolymers were cured with bio-based diamines to produce poly(carbohydrate−urethane) polymers tailored for enabling cure at ambient temperatures and for meeting the demands of coating applications.

EXPERIMENTAL SECTION

Materials. Acrolein 90%, formic acid 95%, *m*CPBA 70−77%, 1-dodecylamine 99%, and dichloromethane 99% were obtained from Sigma-Aldrich. DMSO 99% and peracetic acid 38−40% were obtained from Merck, MMPP 80% from SAF, THF from Carl Roth, TBAB 99% from AlfaAesar, and 2-methyltetrahydrofuran 99% from AppliChem. 1-Octylamine 99% was obtained from Fluka. Carbon dioxide (N45) was obtained from Air Liquid. All deuterated solvents were purchased by Deutero GmbH. Priamine1074 was obtained from Croda GmbH.

Characterization. *ATR-FTIR Spectroscopy.* Fourier transform infrared analysis was made with Vector 22 from Bruker. The attenuated total reflection measurements were recorded by using 30 scans between 4000 and 800 cm^{-1}.

In general, the kinetic studies were made by dissolving the carbonates in DMSO (2 mol/L). The reaction was started by addition of the equimolar amount of the amine species. The zero point was set by mixing the carbonate and the equimolar amount of the alcohol related to the used amine (e.g., ethylene glycol for ethanolamine). The examination of the values were made by relation of the cyclic carbonate (1800 cm^{-1}) to the CH_2 (2925 cm^{-1}) signals.

NMR Spectroscopy. NMR spectroscopy measurements were made with the Avance II spectrometer from Bruker. The spectra were recorded with a frequency of 300 MHz by using different deuterated solvents like acetone-d_6, $CDCl_3$, and DMSO-d_6.

In general, the kinetic studies in the NMR tube were done with the conversion of STC with octylamine. Therefore, STC (0.1 g, 3.8 mmol) was dissolving in DMSO-d_6. Shortly before the measurement was started, octylamine (0.05 g, 3.8 mmol) was added into the NMR tube. For the duration of 9 h, spectroscopic analyses performed every 30 min for ^1H NMR and every 15 min for ^{13}C NMR spectra are included in the Supporting Information.

Evaluation of the conversion rate of external and internal cyclic carbonate groups was determined by the conversion of STC and dodecylamine. Therefore, STC (0.10 g, 3.8 mmol) was dissolved in DMSO-d_6 (1 mL), and dodecylamine (0.71 g, 3.8 mmol) was also dissolved in DMSO-d_6 (1 mL). Both solutions were added into one flask and stirred for 24 h at room temperature. Hence, the product was analyzed by one and two-dimensional NMR experiment. All spectra are included in the Supporting Information.

Thermogravimetric Analysis. Analysis was made with a thermoscale STA 409 (Netzsch). The degradation and the mass loss were detected in a temperature range between 50 and 650 °C under an air atmosphere with a heating rate of 10 K/min.

Differential Scanning Calorimetry. The thermal properties were obtained by using a DSC-1 PerkinElmer and also by Netzsch DSC 204 F1 Phoenix (heating rate 10 or 20 K/min).

Stress−Strain Characterization. Mechanical characterization of casted dog bones was studied by using a Zwick Z005 (Ulm, Germany, ISO527A1, 5 mm/min). The measurement occurred at room temperature. Young's modulus and elongation at break were determined by taking the statistical average of at least five test samples.

***cis*/*trans*-1,2-Divinylethylene Glycol (DVG, 2).** Acrolein (30 mL, 90%, 0.40 mol) was added to a mixture of THF (900 mL) and saturated aqueous ammonium chloride (540 mL). Zinc (52.9 g, 0.808 mol) was added, and the mixture was allowed to stir for 16 h at room temperature.

DOI: 10.1021/acs.macromol.6b01485
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Afterward, the mixture was filtered, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 250 mL). The combined organic phases were dried over magnesium sulfate, and the solvent was removed in a vacuum. The product, a colorless oil (15.5 g, 70%), was purified by vacuum distillation (80 °C and 3 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.5 (br s, 2H, −O*H*), 3.9−3.95 (dd, 4.77 Hz, 1 Hz, 1H, 3-C*H*), 4.10−4.17 (dd, 4.77, 1 Hz, 1H, 4-C*H*), 5.15−5.35 (m, 4H, 1/6-CH_2), 5.75−5.88 (m, 2H, 2/5-CH_2) ppm.

***cis/trans*-1,2-Divinylethylene Carbonate (DVC, 3).** *cis/trans*-1,2-Divinylethylene glycol (DVG, **2**) (15.00 g, 131.4 mmol) was dissolved in diethyl carbonate (19.4 g, 19.9 mL, 164 mmol, 1.25 equiv), and potassium carbonate (0.054 g, 0.395 mmol) was additionally added. The reaction mixture was heated to 115 °C as long as ethanol could be distilled off. As no ethanol development could be detected anymore, the pressure was reduced to 1 mbar and the product (16.0 g, 0.114 mol, 95%) was gained at 105 °C as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): ν = 4.63−4.65 (dd, 2.95 Hz, 6.61 Hz, 1H, 1-C*H*), 5.07−5.13 (dd, 2.95 Hz, 6.61 Hz, 1H, 1′-C*H*), 5.33−5.49 (m, 4H, 3/3′-CH_2), 5.64−5.90 (m, 2H, 2/2′-C*H*) ppm.

Dimethyldioxirane (DMDO). In a two-neck bottle flask water (175 mL), $NaHCO_3$ (29.0 g, 345 mmol), and acetone (96 mL, 75.8 g, 1.31 mol) were stirred and cooled with an ice bath to 5 °C. To this mixture oxone (60 g, 195 mmol) was added in different portions every 3 min. After the last addition the mixture was stirred for an additional 3 min, the ice path was removed, and the pressure was reduced to 100 mbar. The boiling gas was condensed at −78 °C. The resulting yellow liquid was dried over K_2CO_3/molecular sieve (4 Å) and stored at −78 °C.

The concentration of DMDO in the mixture was identified by oxidation of triphenylphosphine (50.2 mg, 0.19 mmol) with 1 mL of DMDO−acetone solution and calculated afterward with the ^{1}H NMR spectroscopy. A concentration of 0.08 mol/L 0.09% of DMDO could be determined.

General Procedure for All Epoxidation Reactions. DVC was dissolved and cooled to 0 °C. To this mixture the oxidant was slowly added in three portions. The crude mixture was first warmed at ambient temperature and then heated to the necessary reaction temperature. The progress was observed by ^{1}H NMR spectroscopy.

*4,5-Diepoxy-2-yl-1,3-dioxolan-2-one (DOC, **4**).* *cis/trans*-1,2-Divinylethylene carbonate (12 g, 0.09 mol) was dissolved in CH_2Cl_2 (120 mL), and the mixture was cooled to 0 °C. *m*CPBA (70−77%, 2.2 equiv, 0.42 mol, 45 g) was added to the mixture in different portions. The mixture was allowed to stir for 5 min at 0 °C. Afterward, the reaction was warmed slowly to 60 °C. The epoxidation process was finished after 3 days reflux at 60 °C.

The precipitated 3-chlorobenzoic acid (*m*CBA) was removed by filtration, and the mother lye was mixed with isohexane (30 mL). Dichloromethane was removed under vacuum, and the remaining mixture of isohexane was stirred for 15 min at 40 °C. The residue was washed over 30 times with fresh isohexane. The product, colorless oil (13.4 g, 0.77 mol, 92%) was gained after removal of residual isohexane in vacuum. ^{1}H NMR (300 MHz, $CDCl_3$): ν = 2.9−3.1 (m, 4H, 1,1′C-H_2), 3.3−3.6 (m, 2H, 2,2′ C-*H*), 4.7−4.8 (m, 1H, 3,3′ C-*H*) ppm.

Sorbitol Tricarbonate (STC, 5). *General Procedure.* In an autoclave, the bisepoxide 4,5-divinyl-2-yl-1,3-dioxolan-2-one (70%) was dissolved and treated with a catalytical amount of 0.5−1 wt % TBAB. The autoclave was fluted with CO_2 to 40 bar, and the mixture was allowed to stir at 80 °C. Afterward, the mixture was cooled down to room temperature The precipitated powder was washed with water and cold acetone. The dried product could be isolated as a slightly beige powder (50%). ^{1}H NMR (300 MHz, acetone-d_6): ν = 4.49 (dd, 2H, C−H_2), 4.53 (t, 2H, C−H_2), 5.1 (m, 2H, C−*H*) ppm.^{13}C NMR (300 MHz, acetone-d_6): ν = 65 (*C*−O), 74 (*C*−O), 76 (*C*═*O*), 154 ppm.

Sorbitol Tricarbonate Made by Transesterification of Sorbitol with Diphenyl Carbonate. D-Sorbitol (50.00 g, 0.274 mol), diphenyl carbonate (3.3 equiv, 193.69 g, 0.904 mol), DMSO (70 mL, 1.1 mol/L), and a catalytic amount of K_2CO_3 (1 mol %, 150 mg) were heated to 120 °C at 30 mbar. During the conversion DMSO and phenol were distilled off very slowly. The residue brown solid product was recrystallized in acetone. The product was isolated as a colorless, crystalline powder (70%).

General Procedure of NIPU Preparation. Sorbitol tricarbonate was mixed with the respective amine at room temperature for 1 min. This mixture was homogenized with a rolling mill at room temperature 2·(90 μm/30 μm), 2·(15 μm/5 μm). The process destroys the crystalline structure of STC and accelerates the forming of STC/diamine prepolymers. The homogeneous resign was degassed at 60 °C for 5 min and casted into a mold. Cure was carried out at 80 °C for 16 h. The conversion of the reaction progress was determined by ATR-FTIR spectroscopy using the appearance of cyclic carbonate groups at 1800 cm^{-1} and the urethane bond at 1700 cm^{-1}.

RESULTS AND DISCUSSION

From Glycerol to Sorbitol Tricarbonate (STC). Following Trost's synthetic procedure (see Scheme 2), acrolein (**1**) was dimerized to produce *cis/trans*-1,2-divinyl ethylene glycol (DVG, **2**), which was converted into the corresponding 1,2-divinyl carbonate (DVC, **3**) by transesterification with diethyl carbonate.[30,31]

Owing to the electron-withdrawing effect of the cyclic carbonate group, the reactivity of the double bonds was rather low with respect to oxidation reactions. Hence, magnesium monoperoxyphthalate (MMPP) and Na_2WO_4/H_2O_2 failed to produce DOC. Albeit both peracetic acid and the more reactive performic acid afforded DVC double-bond conversion at 45 °C, no DOC was detected. According to ^{1}H NMR data, the main products were *α,β*-hydroxy esters, as is evident from the multiplet signal at 4 ppm. Obviously, the harsh reaction conditions and long reaction times caused ring-opening of the epoxy groups to produce esters. Furthermore, this ester formation was confirmed by means of GC/MS analyses. For the first time vinyl group conversion >90%, and successful epoxidation was achieved when using dimethyldioxirane (DMDO) which represents a green non-nucleophilic oxidizing agent, prepared by oxidation of acetone with potassium peroxymonosulfate (Oxone).[32,33] DVC was added to the solution of DMDO and acetone and stirred at room temperature. Even at long reaction time of 48 h, the ^{1}H NMR spectroscopic analysis did not reveal any side-products in DOC formation. In lab synthesis, DMDO was successfully substituted by *m*-chlorobenzoic peracid (mCPBA) which is well-known as highly reactive epoxidation reagent in organic synthesis.[34] Typically, DVC was dissolved in CH_2Cl_2 and cooled to 0 °C. After adding mCPBA, the reaction mixture was allowed to warm up to 60 °C. The reaction progress was observed by ^{1}H NMR spectroscopy (see Figure 1). The signals at 5.33−5.49 ppm (m, 4H, 2/2′-CH_2), 5.64−5.90 ppm (m, 2H, 2/2′-C*H*) correspond to the vinyl groups. With increasing reaction time the intensity of the double bond signals decreased, whereas the signals at 2.9−3.1 ppm (m, 4H, a,a′-CH_2), 3.3−3.6 ppm (m, 2H, b,b′-C−*H*), corresponding to the epoxy groups, increased. Owing to the absence of stereoselectivity, the signals at 4.7−4.8 ppm (m, 1H, c,c′-C−H) corresponding to the hydrogen atoms allocated next to the epoxide and cyclic carbonate groups were broadened. There was no indication for side-reactions. While a reaction time of 1 day at 60 °C gave 50% double-bond conversion, full conversion was observed after 3 days. DOC was formed in essentially quantitative yields as verified by ^{1}H NMR spectroscopy.

The yellowish and highly viscous DOC was purified by column chromatography using a mixture of isohexane and ethyl acetate (60:40) and characterized by means of GC/MS and ^{1}H NMR to further confirm the successful DOC formation. Since DOC was exceptionally reactive and highly sensitive to nucleophiles, DOC did not tolerate the addition of bases used in conventional

DOI: 10.1021/acs.macromol.6b01485
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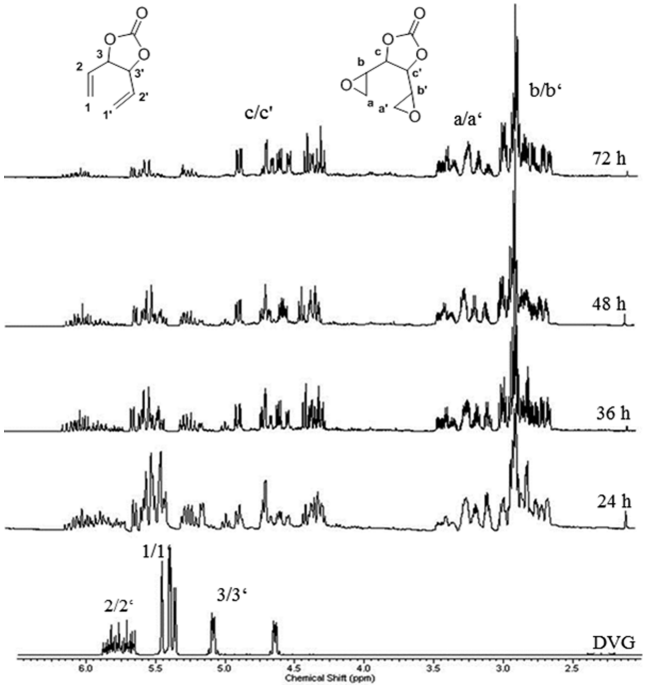

Figure 1. Monitoring the epoxidation of DVC with *m*CPBA at 60 °C by means of ^{1}H NMR spectroscopy ($CDCl_3$).

epoxidation processes to remove 3-chlorobenzoic acid (mCBA). Hence, a base-free method for separating mCBA was developed. Unlike mCBA, DOC was hardly soluble in isohexane. After filtering off the precipitated 3-chlorobenzoic acid, isohexane was added to dichloromethane, which was then distilled off to produce a DOC slurry in isohexane. Extraction with isohexane enabled the complete separation of 3-chlorobenzoic acid. In principle, it is feasible to recycle mCBA and the solvents. The optimized synthesis yielded DOC in 95% yield and purity of 97%. According to thermal analyses by DSC and TGA, DOC decomposed at 195 °C.

As shown in Scheme 2, DOC was converted into STC by catalyzed chemical fixation of CO_2 in the presence of 0.5−1 wt % tetrabutylammonium bromide (TBAB) as catalyst and 40 bar of CO_2 pressure. In green solvents like 2-methyltetrahydrofuran, THF, and DMSO, STC was obtained within 3 days at 60 and 80 °C in quantitative yields. On increasing the temperature above 100 °C, no STC was formed. Using other solvents and K_2CO_3 as catalyst at temperatures above 80 °C failed to produce STC owing to side reactions. The gained products did not contain any epoxide groups which led to the assumption that the side reaction was carried out by the opening of the epoxide rings. Further characterization on byproduct formation was not investigated. In THF or 2-methyltetrahydrofuran pure STC precipitated from the reaction mixture and was readily recovered by filtration. The high purity of STC was confirmed by means of ^{1}H NMR spectroscopy (see Figure 2). STC contains three cyclic carbonate rings. By means of ^{1}H NMR spectroscopy it was possible to distinguish between the internal and the two terminal cyclic carbonate groups. The hydrogen atoms allocated the terminal cyclic carbonates are marked as H_1, H_2, H_3, H_6, H_7, H_8 and correspond to the two signals, at 4.45 ppm (dd, CH_2) and 4.67 ppm (t, CH_2). This coupling is observed, since the rings have different configurations. The hydrogen atoms of the internal cyclic carbonate are marked with H_4, H_5 and correspond to a multiplet signal at 5.20 ppm. The downfield shift is attributed to the electron-withdrawing effect of the adjacent terminal cyclic carbonate rings.

STC is a crystalline solid melting at 230 °C, at which thermal decomposition starts. Moreover, it should be noted that STC is hardly soluble in most common organic solvents with the exception of DMSO, acetone, acetonitrile, and also ionic liquids such as 1-ethyl-3-methylimidazolium acetate and cyclic carbonates such as propylene and ethylene carbonate.

In an alternative synthetic process (see more details in the Supporting Information), high purity STC was also prepared by transesterification of sorbitol with diphenyl carbonate in order to examine the STC stereochemistry. Sorbitol contains asymmetric carbon atoms which dictate the STC configuration. According to NMR spectroscopy, STC derived from glycerol and sorbitol are

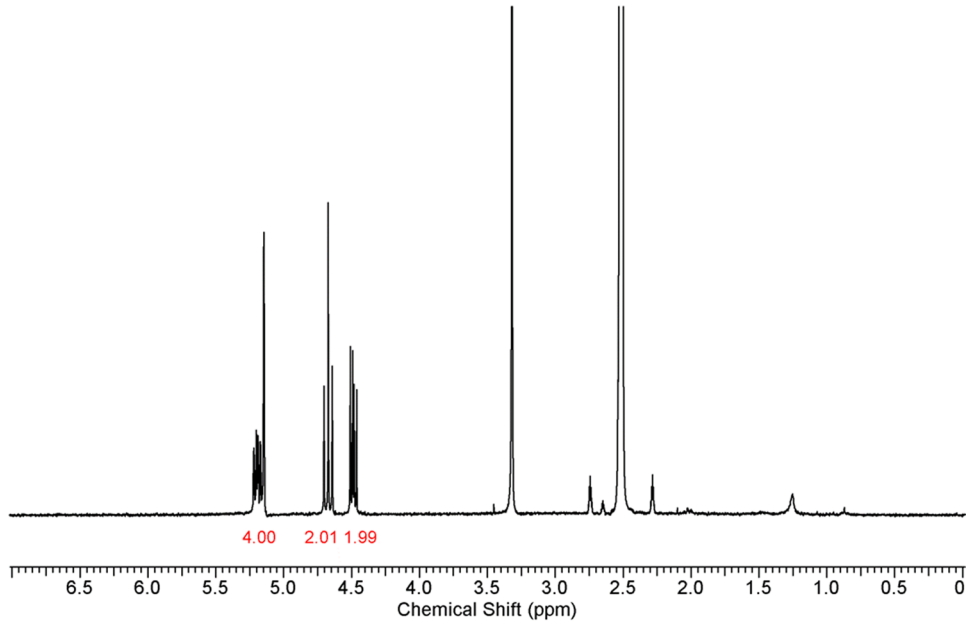

Figure 2. ^{1}H NMR spectrum (DMSO-d_6): sorbitol tricarbonate prepared by chemical fixation of CO_2 from DOC at 60 °C and 40 bar in THF.

DOI: 10.1021/acs.macromol.6b01485
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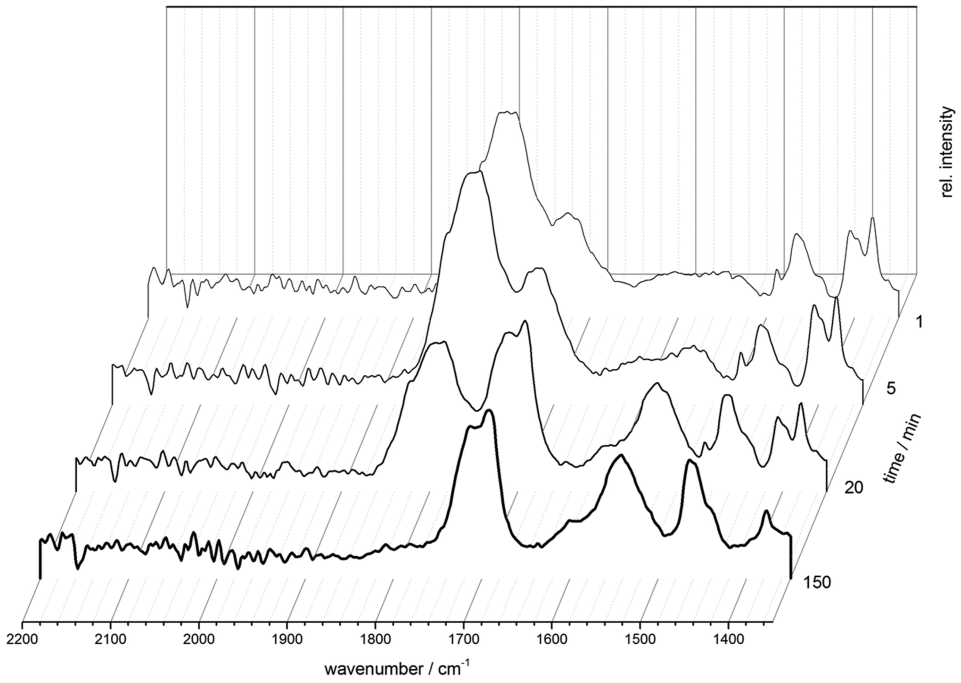

Figure 3. FT-IR spectroscopic study of STC (O═C: 1800 cm^{-1}) bulk conversion with 1-octylamine to produce urethane (O═C: 1700 cm^{-1}) for 1, 5, 20, and 150 min at room temperature.

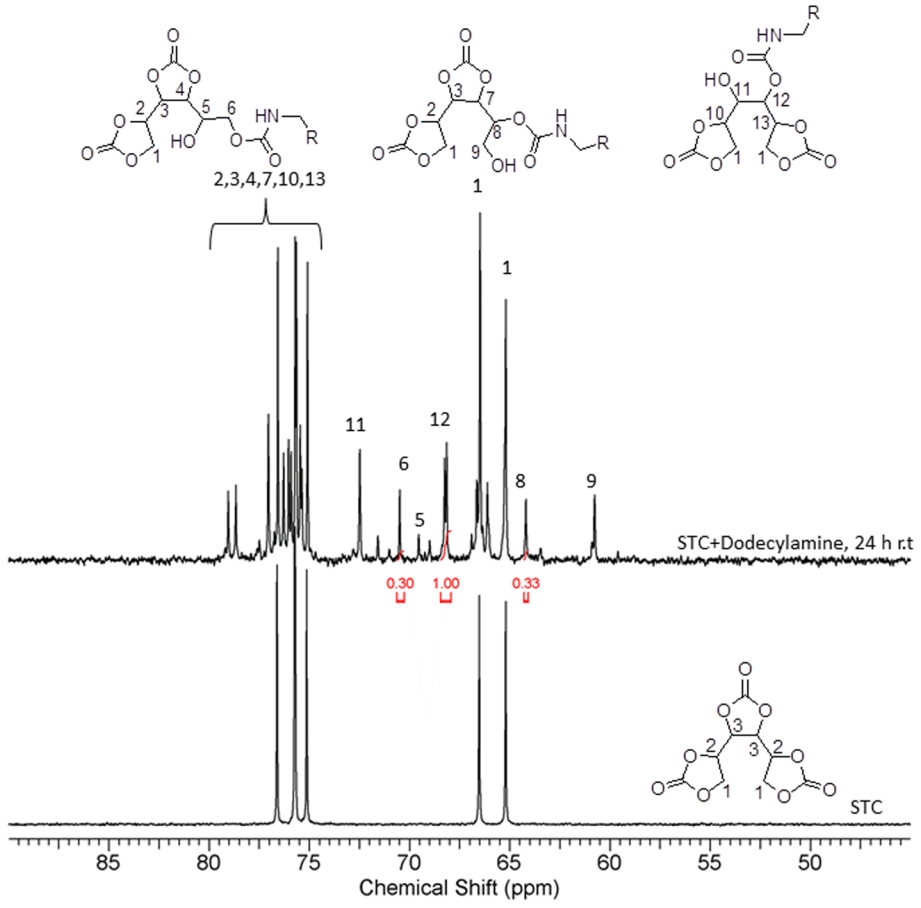

Figure 4. ^{13}C NMR-ig (DMSO-d_6): hydroxyurethanes prepared from sorbitol tricarbonate and 1-dodecylamine at room temperature in DMSO after 24 h.

identical with respect to their chemical shifts but differ with respect to their signal coupling. Most likely, the acrolein route is nonstereospecific, thus affording STC with random placement of the carbonate groups.

DOI: 10.1021/acs.macromol.6b01485
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Reaction of STC with Primary Amines. In general, cyclic carbonates are considerably less reactive than isocyanates and do not allow amine cure at ambient temperatures. This is problematic for many applications.[17,35]

Goldstein et al. investigated the kinetics of aminolysis of erythritol dicarbonate as well as of sorbitol, mannitol, and dulicitol tricarbonates with *n*-butylamine in DMSO.[28] Using the Monte Carlo method to provide the model reaction including the neighboring group effect, they confirmed that adjacent cyclic carbonate groups have an accelerating influence regarding the conversion with primary amines.[28]

In order to examine the role of vicinal cyclic carbonates, the amine reaction of STC was compared with that of ethylene carbonate (EC) and styrene carbonate (SC) by monitoring the reaction using FT-IR and ^{1}H NMR spectroscopy. As is apparent from Figure 3 for the bulk reaction of STC with 1-octylamine, the IR band at 1800 cm^{-1} corresponds to the carbonyl group of the cyclic carbonate rings, whereas the signal at 1700 cm^{-1} corresponds to the urethane group formed by the ring-opening of cyclic carbonates with 1-octylamine.

At room temperature, STC readily reacted with 1-octylamine. Already after 1 min the amine-mediated ring-opening accounted for the formation of urethane groups. After 150 min, the absence of carbonyl groups of cyclic carbonates indicated full STC conversion. To classify the acceleration induced by the neighboring group, model reactions of the aminolysis of STC, EC, and SC with ethanolamine in DMSO solution (2 mol/L) at room temperature were made. DMSO was used as solvent in order to prevent precipitation.

According to the FT-IR spectroscopic analysis, all three cyclic carbonates reacted with ethanolamine at room temperature. However, the reactivity was vastly different, as indicated by the ranking STC ≫ EC > SC. Unlike EC and SC, only STC gave full carbonate conversion after 210 min. Owing to the steric hindrance and the inductive effect of the phenyl group, SC was less reactive. In fact, SC failed to give high conversion even after prolonged reaction times of 800 min. Interestingly, the STC reaction was much faster during the first 10 min and markedly slowed down afterward. In order to examine whether the two different carbonate groups had different reactivities, the aminolysis with 1-dodecylamine was monitored by means of ^{1}H NMR and ^{13}C NMR spectroscopy. Typically, STC and 1-dodecylamine were dissolved separately in DMSO-d_6. Both solutions were joined together in a flask and stirred for 24 h at room temperature to ensure complete conversion. This study confirmed that both internal and terminal carbonate groups reacted with 1-dodecylamine at room temperature.

The rate of the conversion for each carbonate group was calculated from inverse-gated ^{13}C NMR measurements using the signal intensity of the urethane carbon (carbon 12, see Figure 4) signal at 68 ppm, resulting from ring-opening of the internal cyclic carbonate, as compared to the signal intensity of the urethane carbonyl groups at 64 ppm (carbon 8) and 71 ppm (carbon 6), corresponding to the reaction products relating to the ring-opening reaction of the terminal cyclic carbonate groups.

This study (for more details see Supporting Information) revealed that the internal carbonate group reacted more than 3.2 times faster with respect to the terminal ones. The conversion rate was calculated according to eq 1. Hence, the factor of 2 is necessary to include all different types of the formed reaction products. Statistically, it must be taken into account that STC has 2 times more external carbonates than internal ones. Moreover, each of the external groups can produce two different products (8) and (6). The ratio between C_{12} and both carbons C_6 and C_8 multiply by the statistic factor gave the reactivity of the internal cyclic carbonate group.

$$v_{\mathrm{intCO_3}} = \frac{I_{\mathrm{C12,68\ ppm}}}{\frac{1}{2}(I_{\mathrm{C8,64\ ppm}} + I_{\mathrm{C6,71\ ppm}})} = \frac{1}{0.30 + 0.33} \cdot 2 = 3.2 \quad (1)$$

The calculations of initial rates of each carbonate group were not possible by using NMR spectroscopy. Inverse-gated ^{13}C NMR experiments are very slow and cannot display fast conversions as observed for STC with primary amines.

On one hand, in accordance with NMR spectroscopic observations (see Figure 2), the internal cyclic carbonate has a considerably lower electron density compared to its two neighbors and is much more reactive with respect to amine reactions. On the other hand, the internal cyclic carbonate ring is not as sterically hindered as might be expected. This is in accordance with the X-ray structure, which shows that sorbitol tricarbonate crystallizes in the orthorhombic space group $P2_12_12_1$. From this data it is apparent that the internal cyclic carbonate is not shielded but readily accessible (see Figure 5).

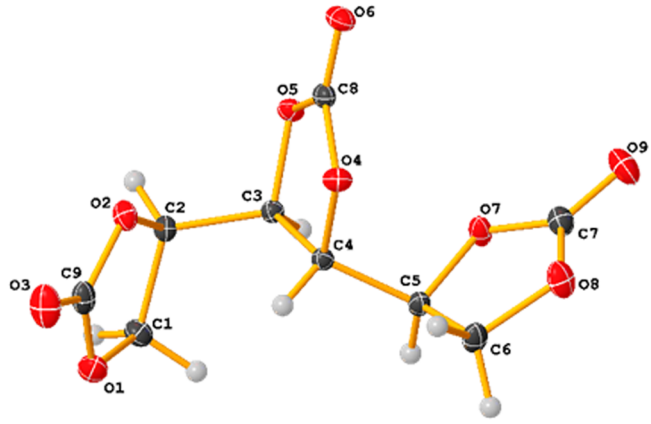

Figure 5. Molecular structure of STC from X-ray diffraction with displacement parameters at 50% probability.

Poly(carbohydrate−urethane) Thermosets by STC Amine Cure. Albeit STC, derived from sorbitol, has been around since many years and affords poly(carbohydrate−urethane) on amine reactions, no attempts have been reported to exploit STC as intermediate for NIPU thermoset formation. This is not surprising since STC is a crystalline solid which is immiscible with most NIPU components. Moreover, the high carbonate functionality accounts for rather short gelation and pot life times together with the formation of densely cross-linked NIPU, assumed to exhibit high stiffness but rather low toughness. Accordingly, cure with short chain diamines such as 1,12-dodecadiamine was rather tedious owing to the extremely narrow processing window, paralleled by short pot life and miscibility problems. Also long-chain nonpolar fatty acid-based diamines as Priamine 1074 are highly immiscible with STC. However, this severe immiscibility problem was solved by forming of STC/Priamine prepolymers in a three-roll mill. Unlike crystalline STC, the resulting prepolymer were liquids, fully miscible with various amine curing agents. Taking into account that cross-linking readily progressed at room temperature on mixing prepolymer with the amine curing agent, degassing and casting

DOI: 10.1021/acs.macromol.6b01485
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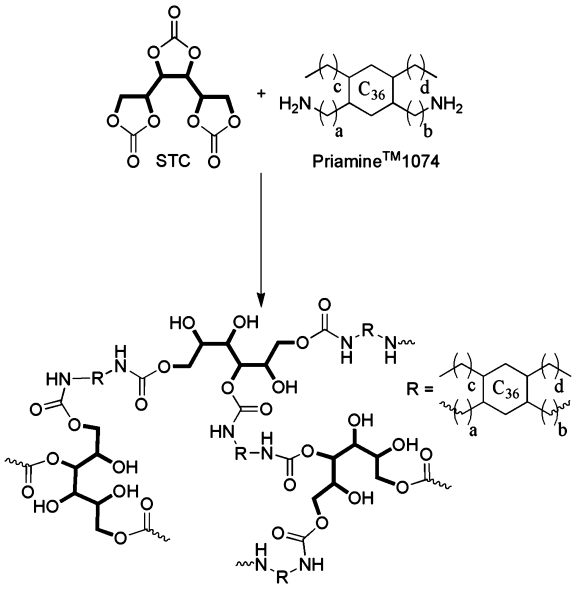

Figure 6. Poly(carbohydrate–urethane) structures obtained by curing STC prepolymer with dimer-fatty-acid-derived diamine (Priamine 1074).

were performed within 5 min. Figure 6 displays the poly(carbohydrate–urethane) network structure containing highly rigid sorbitol-based segments together with highly flexible segments corresponding to the incorporation of the dimer-fatty-acid-based diamine. This balance of rigid and flexible segments enabled tailoring of poly(carbohydrate–urethane) mechanical properties ranging from highly stiff to soft as well as from brittle to flexible and elastomeric.

Table 1 summarizes the mechanical and the thermal properties of poly(carbohydrate–urethanes) prepared by curing STC with blends of Priamine 1074 and isophorone diamine (IPDA) with variable IPDA content. Poly(carbohydrate–urethanes) represent a novel generation of 100% bio-based NIPU materials.

Table 1. Thermal and Mechanical Properties of STC-Based Poly(carbohydrate–urethanes) as a Function of the Priamine 1074/Isophorone Diamine (IPDA) Blend Ratio

Priamine 1074 [mol %]	IPDA [mol %]	T_g[b] [°C]	Young's modulus[c] [MPa]	elongation at break[c] [%]
100	0	29	12.0 ± 1.0	250 ± 10
70	30	39	220 ± 20	2.5 ± 0.5
60	40	50	480 ± 40	5.0 ± 2.0
40	60	60	630 ± 40	0.30 ± 0.03

[a]Processing: homogenization and STC prepolymer formation in a three-roll mill at rt; curing: 16 h, 80 °C. [b]DSC: 20 K/min. [c]ISO 527A1.

Unlike brittle poly(carbohydrate–urethanes), formed by curing STC prepolymers with short chain diamines, the STC prepolymer formation and cure with flexible Priamine 1074 afforded highly flexible and soft poly(carbohydrate–urethane) thermosets exhibiting low glass temperature of 29 °C and low stiffness as reflected by Young's modulus of only 12 MPa, paralleled by high elongation at break of 250%. The stiffness of poly(carbohydrate–urethane) thermosets increased substantially by blending highly flexible diamines together with rigid diamines such as isophorone diamine (IPDA). As a function of the IPDA content, the Young's modulus increased to 630 MPa (+5000%!) and the glass temperature to 60 °C (+200%), accompanied by drastically lowered elongation at break. Poly(carbohydrate–urethanes), prepared by curing STC prepolymer with a blend of 40 mol % IPDA and 60 mol % Priamine 1074 were attractive materials regarding coating applications. According to the TGA analysis, all casted materials showed the same thermal stability with the onset temperatures of T_1 = 190 C and T_2 = 420 °C.

The prepolymer blend with the amine curing agent was coated onto a glass plate using a coating knife and cured at 80 °C for 14 h. Unlike many other NIPU coatings, fully transparent, colorless, and scratch resistant coatings were formed (see Figure 7). The contact angle of water of 101° indicated that the incorporation of flexible dimer-fatty-acid-derived segments rendered the hydrophilic poly(carbohydrate–urethane) hydrophobic.

CONCLUSION

Sorbitol tricarbonate (STC), traditionally prepared by phosgenation of sorbitol, has been known since many years but requires tedious purification. Its limited availability in conjunction with high melting temperature over 200 °C close to its decomposition temperature, extremely poor solubility, and immiscibility with the majority of amine curing agents have prevented its application in polymer industry. In our research we have successfully established glycerol- and sorbitol-based synthetic strategies to produce high purity STC and STC prepolymers as well as the corresponding poly(carbohydrate–urethane) thermosets and coatings. Poly(carbohydrate–urethanes), prepared by amine cure, represent as new class of 100% bio-based nonisocyanate polyhydroxyurethane materials (NIPU). In addition to our green phosgene-free carbonatization of sorbitol by means of sorbitol transesterification with diphenyl carbonate, for the first time we gain STC from glycerol feedstock. Unlike sorbitol and other saccharides, glycerol is an abundant industrial byproduct of biodiesel production and allows to reuse industrial waste products. In our glycerol-based STC synthesis, acrolein, industrially available by oxidation of glycerol, is dimerized and carbonated by means of transesterification with diethyl carbonate. The resulting 1,2-divinylethylene carbonate (DVC)

Figure 7. Colorless and optically transparent poly(carbohydrate–urethane) coating derived from STC and Priamine 1074/IPDA (40 mol %/60 mol %).

DOI: 10.1021/acs.macromol.6b01485
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is then oxidized to produce the new and highly reactive 4,5-diepoxy-2-yl-1,3-dioxolan-2-one (DOC) in high yields and with high purity. Finally, two terminal cyclic carbonate groups are attached to the cyclic carbonate moiety by catalytic carbonatization of DOC with CO_2. The FT-IR and NMR spectroscopic investigation of STC model reactions with monoamines such as 1-octylamine and ethanolamine reveals that full amine conversion is achieved at ambient temperature, thus producing poly(carbohydrate−urethanes) in essentially quantitative yields. Opposite to the existing dogma in NIPU chemistry that terminal carbonate groups are always more reactive with respect to internal carbonate groups, our NMR model study clearly confirms that the internal carbonate is 3 times more reactive as compared to the terminal cyclic carbonate groups. On one hand, this behavior is attributed to the electron-withdrawing substituent effect of the terminal cyclic carbonates, as verified by the downfield shifts of the ^{1}H NMR signals corresponding to methine groups of the internal cyclic carbonate rings. On the other hand, according to the X-ray structure analysis of STC, the steric hindrance of the internal cyclic carbonate group is much lower than expected. Moreover, although STC has rather low solubility, it is rendered miscible with nonpolar amine curing agents such as the dimer-fatty-acid-derived diamine (Priamine 1074) by prepolymer formation. Typically, the advancement reaction of diamine with STC prior to the subsequent cure with the stoichiometric amount of diamines produces a liquid prepolymer which is fully miscible with a great variety of other amine curing agents. As a function of the diamine blend ratio of rigid IPDA and highly flexible Priamine 1074 the poly(carbohydrate−urethanes) properties vary from highly rigid and stiff to flexible, elastomeric, and even ultrasoft. Moreover, the STC-prepolymer-mediated cure with blends of flexible and rigid diamines affords optically transparent, colorless, and scratch-resistant 100% bio-based polyhydroxyurethane coatings. In summary, both glycerol- and sorbitol-based STC and especially the corresponding STC prepolymers represent versatile intermediates for preparing multifunctional carbohydrate-like polyurethanes and 100% bio-based polyurethanes tailored for meeting the diversified applications ranging from coatings and adhesives to foams and biomedical applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01485.

Experimental details (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the support by JONAS−Joint Research Network on Advanced Materials and Systems, BASF SE, Ludwigshafen, Germany, and the Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg, Stuttgart, Germany. We also thank Ellen Günther, Hannes Blattmann Dr. Christian Bühler, Dr. Gemma Sanders, and Dr. Kimberly Simancas for their valuable assistance and helpful advice.

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