Tunable Poly(hydroxyl urethane) from CO₂-Based Intermediates Using Thiol-Ene Chemistry

CHAU N. TANG,¹ HUNAID B. NULWALA,¹ KRISHNAN DAMODARAN,² PALWINDER KAUR,³ DAVID R. LUEBKE¹

¹National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, Pennsylvania 15236

²Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

³Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received 23 December 2010; accepted 10 February 2011 DOI: 10.1002/pola.24631 Published online 9 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: CO_2 -based, crosslinked poly(hydroxyl urethane)s (PHUs) are accessed via a set of efficient reactions based on the addition chemistry of thiol-ene and amines-cyclic carbonates. This strategy to utilize 5-membered cyclic carbonates produced from CO_2 is robust, facile, modular, and atomically efficient in nature. The thiol-ene reaction was utilized to access bis(cyclic carbonate), tris(cyclic carbonate), and tetrakis(cyclic carbonate) in quantitative yield from 4-vinyl-1,3-dioxolan-2-one and thiols. Multi-functional cyclic carbonates were simply mixed with diethylenetriamine and/or 1,6-diaminohexane to

generate crosslinked PHUs from 25 to 80 °C. These materials are easy to scale-up and are potential candidates in many applications such as coatings, binders, and resins. The resulting polymers have glass transition temperatures between -1 and 16 °C and thermal decomposition temperatures from 190 to 230 °C. © 2011 Wiley Periodicals, Inc.[†] J Polym Sci Part A: Polym Chem 49: 2024–2032, 2011

KEYWORDS: amine; carbonate; crosslinked polyurethanes; poly-(hydroxyl urethane)s; thiol-ene chemistry

INTRODUCTION The observed increase in atmospheric CO₂ concentration since the beginning of the industrial era is mainly due to the burning of fossil fuels.¹ This increase in CO₂ concentration is believed to be the major cause of global warming.²⁻⁴ To stave off potentially serious changes in the global climate, it is important to stabilize the CO_2 levels in the atmosphere. A major effort will be required to reduce CO₂ emissions.⁵ Complete replacement of fossil fuels with renewable energy sources in the short term is probably not feasible; therefore, a program of CO₂ capture followed by geological storage or utilization is necessary. There is a need to develop processes and reactions to efficiently store and utilize CO_2 . The captured CO_2 may be thought of as the cheapest raw material available for the development of polymers, pharmaceuticals, solvents, and other products. Although the scales of production of these materials are not sufficient to entirely make use of the CO₂, the transformation of CO₂ into useful products can decrease the volume which must be sequestered and generate revenues to offset the cost. Many authors have focused on the development of CO₂based materials via the direct and indirect utilization of CO₂.^{6–10}

Though CO_2 is cheap, abundant, and non-toxic, it has found relatively few uses in industrial processes since it is challenging to develop chemistry which can activate the highly oxidized carbon dioxide and transform it into useful products. CO_2 has strong affinity toward nucleophiles and electrondonating reagents. This makes CO_2 an "anhydrous carbonic acid," which rapidly reacts with basic compounds. For example, organometallic reagents such as Grignard reagents readily react with CO_2 even at a low temperature. Similarly, water, alkoxides, and amines also undergo addition with CO_2 to produce compounds with a carboxyl or carboxylate group. These reactions conveniently produce carbonic and carbamic acids.

Specifically, organic carbonates have applications in thermoplastics,¹¹ thermosets,⁸ electronics^{12,13} (i.e., electrolytes in lithium ion battery and sealant), coatings,^{14–17} solvents, fuel additives,^{13,18} and they are used as starting materials for the preparation of polyurethanes.^{7,19} The formation of organic carbonates is an inexpensive method which has been widely studied for CO₂ fixation. As carbonates have three oxygen atoms in each molecule, they are relatively suitable synthetic targets for CO₂ fixation.²⁰ Five- and six-membered cyclic carbonates are commercially available and are produced from CO₂ in high yields.^{13,21–23} Figure 1 shows several synthetic pathways to produce five-membered cyclic carbonate via cycloaddition of CO₂ and other conventional routes.^{20–22,24–41} These cyclic carbonates have found uses in cycloaddition reaction, but due to their stability, 5-membered cyclic carbonates are more commonly used as solvent.

Poly(hydroxyl urethane)s (PHU) presents an opportunity to directly make polymers from CO_2 -derived precursors. The polyaddition of 5-membered and 6-membered bis(cyclic carbonate)s

Additional Supporting Information may be found in the online version of this article. Correspondence to: D. R. Luebke (E-mail: david.luebke@netl. doe.gov) or H. B. Nulwala (E-mail: hunaid.nulwala@or.netl.doe.gov)

Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 2024–2032 (2011) © 2011 Wiley Periodicals, Inc. [†]This article is a U.S. Government work, and as such, is in the public domain in the United States of America.



FIGURE 1 Reported synthetic routes to produce cyclic carbonates.

with amines has been reported in the literature^{7,19} to obtain PHUs. These polymeric materials have found a wide variety of applications as adhesives, binders, hydrophilic coatings,⁴² hydrogels, and resins. Materials derived from carbonates offer the additional advantage of being environmentally friendly.⁴³

Herein, we present crosslinked PHUs which are easily accessible and tunable from commercially available carbonates and amines. The crosslinked PHUs are accessed via a modular and facile reaction between amines and multi-functional cyclic carbonates, which are prepared from thiol and ene derivatives. Both reactions are atomically efficient and produce solid materials in high yields. The developed synthetic route is facile and represents a less-toxic, non-isocyanate pathway to obtain polyurethanes. The reaction was scaled up to multigram quantities without any need for special equipment or precaution. The approach allows various properties to be tuned such as glass transition temperature, modulus, and content of hydroxyl compounds, which are useful to prepare polymers for targeted applications. The synthesis of 5- and 6membered bis(cyclic carbonate)s using thiol-ene chemistry and linear PHUs had been reported by Endo et al.⁷ The synthesis of crosslinked PHUs in a single step without solvents is reported here for the first time. The multi-functional carbonates were accessed via thiol-ene chemistry, which was inspired by previous experience and the works of many authors who used facile, robust, and modular reactions.44-66 These multi-functional cyclic carbonates can serve as monomers, crosslinkers for polymeric materials with terminal and/ or pendant amines, coupling agents, and compatibilizers.

EXPERIMENTAL

Materials

Diethylenetriamine (DETA), 4-vinyl-1,3-dioxolan-2-one (99%), 1,6-hexanedithiol (>97%), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate) (97%), 1,6-diaminohexane (98%), and 2,2-dimethoxy-2-phenylacetophenone (99%) were used as received from SigmaAldrich. Lithium bromide, octylamine, and a Spectroline UV lamp (Model ENF-280C, 8W) were acquired from Fisher Scientific. Chloroform-d (CDCl₃) was purchased from Cambridge Isotope Laboratory.

Methods

¹H (500 or 700 MHz) and ¹³C (126 or 176 MHz) NMR spectra were recorded in CDCl₃ on a Bruker Avance III 500 or 700 spectrometer. Fourier transform infrared (FT-IR) spectra were measured using a Nicolet IR100 FT-IR spectrometer, equipped with an attenuated total reflectance (ATR) accessory with a diamond crystal. A Mettler Toledo TGA/DSC 1 was used to measure the decomposition temperature, which was determined as 5% mass loss, at a heating rate of 10 °C/min under nitrogen. A TA Instruments Q200 differential scanning calorimeter equipped with the Refrigerated Cooling System 40 accessory was used to determine glass transition temperatures (T_g s), which are taken as the mean of the second and third heating scans. The experiments were conducted under nitrogen at a heating rate of 10 °C/min.

Mass spectroscopy was performed using an Agilent 6420 Triple Quadrupole (QQQ) LC-MS/MS (Agilent Technologies, Santa Clara, CA). Agilent Mass Hunter software (Version B.02.01) was used for data acquisition and processing. The samples were directly infused into the mass spectrometer and eluted at 0.4 mL/min using ethyl acetate. The flow rate of the drying gas (N₂) was 11 L/min, and the gas temperature was 350 °C. The MS fragmentor voltage was fixed at 250 V.

Synthesis of 4,4'-((Hexane-1,6-diylbis(sulfanediyl))bis-(ethane-2,1-diyl))bis(1,3-dioxolan-2-one) (Bis-CC)

2,2-Dimethoxy-1,2-diphenylethanone (0.200 g, 0.780 mmol), 4-vinyl-1,3-dioxolan-2-one (10.2 g, 89.4 mmol), and hexane-1,6-dithiol (6.57 g, 43.7 mmol) were added to an aluminum pan. The mixture was irradiated for 1 h using a UV lamp (365 nm). The conversion was quantitative as confirmed using either GC analysis, ¹H NMR, or FTIR spectroscopy. The product was used without further purification. ¹H NMR (700 MHz, CDCl₃, δ): 1.36 (dt, $J_1 = 7.25$ Hz, $J_2 = 3.63$ Hz, CH_2 , 4H), 1.47-1.59 (m, CH₂, 4H), 1.85-1.95 (m, CH₂, 2H), 2.02-2.14 (m, CH_2 , 2H), 2.49 (t, $J_1 = 7.25$ Hz, S– CH_2 , 4H), 2.54–2.61 (m, S-CH₂, 2H), 2.61-2.71 (m, S-CH₂, 2H), 4.09 (dd, $J_1 = 8.67$ Hz, $J_2 = 7.09$ Hz, O–CH₂, 2H), 4.56 (dd, $J_1 = 8.67$ Hz, $J_2 =$ 7.09 Hz, O—CH₂, 2H), and 4.86 (qd, $J_1 = 7.78$ Hz, $J_2 = 4.41$ Hz, O—CH, 2H). ¹³C NMR (176 MHz, CDCl₃, δ): 27.11 (S—CH₂), 28.30 (S-CH₂), 29.31 (CH₂), 32.23 (CH₂), 33.93 (CH₂), 69.30 (0-CH₂), 75.71 (0-CH(CH₂)₂), and 154.8 (C=O). ATR-IR (cm⁻¹): 466, 714, 770, 1054, 1155, 1378, 1437, 1779 (C=O), 2854, and 2927. MS (*m/z*): calcd for C₁₆H₂₆O₆S₂, 378.12; found, 401.11 [M+Na]⁺.

Synthesis of 2-Ethyl-2-(((3-((2-(2-oxo-1,3-dioxolan-4-yl)ethyl)thio)propanoyl)oxy) methyl)propane-1,3-diyl bis(3-((2-(2-oxo-1,3-dioxolan-4-yl)ethyl)thio)propanoate) (Tris-CC) The procedure was the same as above using trimethylolpropane tris(3-mercaptopropionate) (6.70 g, 16.8 mmol), 4-vinyl-1,3-dioxolan-2-one (5.85 g, 51.3 mmol), and 2,2dimethoxy-2-phenylacetophenone (12.5 mg, 48.8 μmol). ¹H NMR (500 MHz, CDCl₃, δ): 0.88 (t, $J_1 = 7.41$ Hz, CH_3CH_2 , 3H), 1.48 (q, $J_1 = 7.36$ Hz, CH_3CH_2 , 2H), 1.88 – 1.96 (m, CH_2 , 3H), 2.00 – 2.17 (m, CH_2 , 3H), 2.46 – 2.66 (m, CH_2 , 6H), 2.66 – 2.78 (m, CH_2 , 12H), 4.03 (br. S, O— CH_2C , 6H), 4.10 (t, $J_1 =$ 8.50 Hz, O— CH_2CH , 3H), 4.57 (t, $J_1 = 8.35$ Hz, O— CH_2CH , 3H), and 4.87 (qd, $J_1 = 7.83$ Hz, $J_2 = 4.26$ Hz, O— CH_2 CH, 3H), and 4.87 (qd, $J_1 = 7.83$ Hz, $J_2 = 4.26$ Hz, O— CH_3 , 3H). ¹³C NMR (126 MHz, CDCl₃, δ): 7.46 (CH_3), 23.03 (CH_2CH_3), 27.11 (S— CH_2), 27.26 (S— CH_2), 33.79 (CH_2), 34.56 (CH_2 —C=0), 40.84 (CCH_2CH_3), 64.00 (CH_2CO_2), 69.29 (OCH_2CH), 75.58 (OCH_2CH), 154.8 (CO_3), and 171.4 (CH_2CO_2). ATR-IR (cm⁻¹): 468, 714, 770, 1055, 1153, 1236, 1286, 1352, 1382, 1476, 1725 (OC=0), 1783 ($O_2C=0$), 2926, and 2962. MS (m/z): calcd for C₃₀H₄₄O₁₅S₃, 740.18; found, 763.18 [M+Na]⁺.

Synthesis of 2,2-Bis(((3-((2-(2-oxo-1,3-dioxolan-4-yl)ethyl)thio)propanoyl)oxy) methyl)propane-1,3-diyl bis(3-((2-(2oxo-1,3-dioxolan-4-yl)ethyl)thio)propanoate) (Tetra-CC)

The procedure was the same as above using pentaerythritol tetrakis(3-mercaptopropionate) (8.40 g, 17.2 mmol), 4-vinyl-1,3-dioxolan-2-one (7.95 g, 69.6 mmol), and 2,2-dimethoxy-2-phenylacetophenone (11.9 mg, 46.4 μ mol). ¹H NMR (500 MHz, CDCl₃, δ): 1.89 – 1.96 (m, CH₂, 4H), 2.04 – 2.11 (m, CH₂, 4H), 2.58 – 2.65 (m, CH₂, 12H), 2.69 – 2.78 (m, CH₂, 12H), 4.09 – 4.16 (m, 12H), 4.58 (t, J_1 = 8.35 Hz, OCH₂CH, 4H), and 4.87 (qd, J_1 = 7.88, J_2 = 4.41 Hz, OCH₂CH, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 27.06 (S–CH₂), 27.25 (S–CH₂), 33.74 (CH₂), 34.47 (CH₂–C=0), 42.21 [(CH₂)₄–C], 62.36 (CH₂CO₂), 69.31 (OCH₂CHO), 75.63 (OCH₂CH), 154.9 (CO₃), and 171.3 (CH₂CO₂). ATR-IR (cm⁻¹): 714, 769, 1054, 1154, 1236, 1352, 1382, 1478, 1728 (OC=O), 1781 (O₂C=O), 2926, and 2962. MS (*m*/*z*): calcd for C₃₇H₅₂O₂₀S₄, 944.19; found, 967.18 [M+Na]⁺.

Model Reaction

Bis-CC (0.539 g, 1.42 mmol) and octylamine (0.381 g, 2.95 mmol) were added to a 40 mL vial. The mixture was placed into an oil bath at 80 °C for 21 h. Because of the possibility of four isomeric products, the assignment for the ¹H NMR listed only the methyl group and the methylene unit connected to the nitrogen atom; similarly, only the methyl, CH₂N, and carbonyl resonances in the ¹³C NMR were provided. ¹H NMR (500 MHz, CDCl₃, δ): 0.88 (t, J = 6.78 Hz, CH_3 , 6H) and 3.16 (q, J = 6.83 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 14.22 (CH_3), 41.26 (CH_2 NH), and 156.9 (NC=0). ATR-IR (cm⁻¹): 540, 722, 776, 1042, 1141, 1250, 1458, 1536, 1668 (C=0), 2852, 2921, and 3296 (OH and NH).

The reaction was also conducted using a catalyst. Bis-CC (0.533 g, 1.41 mmol), octylamine (0.390 g, 3.02 mmol), and LiBr (21.4 mg, 0.246 mmol) were added to a 40 mL vial. The reaction was placed into an oil bath at 80 $^{\circ}$ C for 2 h.

General Procedures for the Preparation of Poly(hydroxyl urethane)s

In a typical example, an equimolar of total reactive groups from a carbonate (Bis-CC, Tris-CC, and Tetra-CC) and amine(s) were added to a vial containing a stir bar. The reaction was heated at 80 $^{\circ}$ C for the desired amount of time and allowed to cool to room temperature. The crosslinked poly-

(hydroxyl urethane)s (PHUs) were characterized by ATR-IR spectroscopy and thermal analyses.

PHU-1s were synthesized from Bis-CC (0.583 g, 1.54 mmol) and DETA (0.166 g, 1.61 mmol) without a catalyst for 24 and 72 h and with LiBr as a catalyst for 48 h. In addition, the polyaddition of Bis-CC and DETA was conducted at room temperature for 24 h. The mixture became viscous after several hours.

PHU-2 was synthesized from Tris-CC (1.18 g, 1.60 mmol) and DETA (0.180 g, 1.75 mmol) without a catalyst for 24 h.

PHU-3 was synthesized from Tetrakis-CC (1.154 g, 1.22 mmol) and DETA (0.174 g, 1.69 mmol) without a catalyst for 24 h.

The polymerization of Bis-CC and 1,6-diaminohexane using 10 and 24 mol % DETA (mole ratio of DETA to cyclic carbonate) were conducted for 24 h to generate PHU-4a and PHU-4b, respectively. For example, PHU-4a was produced from Bis-CC (1.143 g, 3.02 mmol), 1,6-diaminohexane (0.247 g, 2.13 mmol), and DETA (74.4 mg, 0.721 mmol).

RESULTS AND DISCUSSION

Monomer Syntheses

Thiol-ene chemistry was employed as the general synthetic route to produce CO_2 -based multi-functional cyclic carbonates. This chemistry is appealing due to the robust and orthogonal nature of the reaction and the synthetically powerful characteristics such as lack of byproducts, quantitative yields, and optional use of solvents. In addition, it offers the ability to construct multiple chemical intermediates from commercially available reagents by changing the thiol-ene combination. We chose 4-vinyl-1,3-dioxolan-2-one (VEC), which has been extensively explored in the literature,^{9,29–32} as the CO_2 -based starting material due to its availability and synthetic attributes such as high yield and abundant catalyst selection.

Following the synthetic route outlined in Scheme 1, we demonstrated that bis(cyclic carbonate) (Bis-CC), tris(cyclic carbonate) (Tris-CC), and tetrakis(cyclic carbonate) (Tetra-CC) were successfully synthesized using the thiol-ene reaction of VEC with 1,6-hexanedithiol, trimethylolpropane tris(3-mercaptopropionate), or pentaerythritol tetrakis(3-mercaptopropionate), respectively, at room temperature under UV light using 2,2-dimethoxy-2-phenylacetophenone as an initiator. These multi-functional cyclic carbonates were characterized by FTIR, ¹H NMR, ¹³C NMR, and mass spectroscopies. Figure 2 shows the ¹H NMR spectra of starting reagents (1,6-hexanedithiol and VEC) and Bis-CC after the reaction. In every thiol-ene reaction, the conversion of the limiting reagent (thiols in all of the reactions) was quantitative after a short period (30-60 min) of exposure to UV light. For example, we observed the disappearance of the S-H resonance (1.31) ppm) and a shift of the S– CH_2 resonance (2.49 ppm) in Figure 2 for the reaction between 1,6-hexanedithiol and VEC after 30 min. ¹H NMR spectra of the Bis-CC shows new peaks for the $CH-CH_2-CH_2$ resonance (1.93 and 2.14 ppm), for the $-CH_2-S-CH_2$ resonance (2.54 ppm), for the $-CH_2$ -S-CH₂ resonance (2.64 and 2.72 ppm), and for the



SCHEME 1 Synthetic route to multi-functional cyclic carbonates via thiol-ene reaction of 4-vinyl-1,3-dioxolan-2-one with several thiols.

CH resonance (4.86 ppm) of the cyclic carbonate. ¹H NMR spectra of Tris-CC and Tetra-CC are provided in the Supporting Information as Figures S1 and S2, respectively.

Figure 3 shows the FTIR spectra of VEC, Bis-CC, Tris-CC, and Tetra-CC. The v(C=0) vibration of Bis-CC is at 1779 cm⁻¹. In the case of Tris-CC, the peaks at 1725 and 1783 cm⁻¹ are assigned to the v(C=0) vibrations of the ester and carbonate linkages, respectively. Similarly, the carbonyl groups of the ester and carbonate linkages for Tetra-CC appear at 1728



FIGURE 2 ¹H NMR spectra of 4-vinyl-1,3-dioxolan-2-one (top), 1,6-hexanedithiol (middle), and bis(cyclic carbonate) (bottom).

and 1781 cm^{-1} , respectively. In all of the multi-functional cyclic carbonate, we observed the disappearance of the vibrations due to the vinyl group (942 and 986 cm^{-1}).

To investigate the potential of side reactions, a equimolar mixture of propylene carbonate and 1,6-hexanedithiol was subjected to the same conditions as the thiol-ene reaction (UV irradiation for 1 h) and the polyaddition (80 °C for 24 h). If the thiol undergoes addition with the cyclic carbonate during these experiments, then the product is a thio-carbonate. However, no thiocarbonate was produced for both conditions as confirmed by ¹H NMR spectroscopy (see Fig. S3 of the Support Information). The results further demonstrated the modularity of the chemistry.

Model Reaction

To increase our understanding of the carbamate formation, we reacted octylamine with Bis-CC in the presence and absence of LiBr as a catalyst to generate the urethane DOU. Scheme 2 shows only one of four possible isomeric products for this reaction. The conversion at 80 °C for the uncatalyzed reaction was quantitative after 21 h, and it was quantitative after 2 h for the catalyzed reaction. These observations are similar to results obtained in the literature.^{15,67-69} Besides LiBr, other catalysts such as lithium oxide,⁶⁷ lithium methoxide,⁶⁷ and potassium *t*-butoxide^{15,67} are effective for the addition of carbonates and amines. Carbamate formation was confirmed via FTIR and NMR spectroscopies. Figure 4



FIGURE 3 FTIR spectra of (top to bottom) 4-vinyl-1,3-dioxolan-2-one, bis(cyclic carbonate), tris(cyclic carbonate), and tetrakis-(cyclic carbonate).

compares the FTIR spectra of Bis-CC and DOU. The v(C=0) vibration shifted to a lower wavenumber when the cyclic carbonate linkage (1779 cm⁻¹) was converted into the urethane linkage (1688 cm⁻¹). Furthermore, there are peaks for the carbamate that appears at 1250 and 1536 cm⁻¹ for the N—H bending and C—N stretching and at 3296 cm⁻¹ for N—H and OH stretchings. Endo et al.⁶⁸ reported that the v(C=0) and v(N—H) vibrations are at around 1700 and 3240 cm⁻¹, respectively, for the urethanes produced from hexylamine with different cyclic carbonates. The v(C=0) vibration appear at higher wave number. Similarly, the ¹H NMR spectra (Fig. 5) shows the disappearance of the methylene and ethane moieties from the cyclic carbonate ring and



SCHEME 2 The reaction between bis(cyclic carbonate) and octylamine with and without LiBr as a catalyst (note: scheme shows only one of four isomeric products).



FIGURE 4 FTIR spectra of bis(cyclic carbonate) (top) and DOU (bottom).

the appearance of a methyl group at 0.89 ppm and a CH_2 —N resonance at 3.19 ppm.

Polymerization

In the previous section, we have exploited thiol-ene chemistry to make CO_2 -based multi-functional cyclic carbonates. To study their thermal properties and to identify potential application of the polymers, we conducted the ring-opening polyadditions of Bis-CC, Tris-CC, and Tetra-CC with DETA for 24 h at 80 °C to generate CO_2 -based, crosslinked PHU-1, PHU-2, and PHU-3 (Scheme 3), respectively. Many authors^{6,19} have prepared linear PHUs from bis-functional cyclic carbonates and diamines. All of the polymerizations were performed in bulk to avoid solvent trapping and elaborate the facile nature of this chemistry. These PHUs were characterized using FTIR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

The polymerizations of Bis-CC and DETA were performed with and without LiBr as a catalyst to evaluate the polymerization behavior of this materials. Figure 6 shows the FTIR spectrum of crosslinked PHU-1 as well as those for DOU and crosslinked PHU-4. In PHU-1, hydroxyl urethane linkages are observed at 1690 cm⁻¹ for the C=O stretching and at 3305 cm⁻¹ for the N—H and OH stretchings whereas the v(C=O) vibration of cyclic carbonate in the crosslinked polymer is at 1794 cm⁻¹. Under similar conditions, it was found, as



FIGURE 5 ¹H NMR spectra of bis(cyclic carbonate) (top) and bis-urethane (bottom).



SCHEME 3 Synthetic route to CO₂-based, crosslinked poly(hydroxyl urethane)s.

expected, that materials without LiBr take longer to polymerize than those in which the catalyst was present; however, the former materials have slightly higher $T_{\rm d}$. For example, when the catalyzed polymerization was monitored with FTIR at 4, 24, and 48 h, the v(C=0) vibration of the cyclic carbonate decreased relative to the intensity of the carbonyl stretching due to the urethane linkage. In addition, the intensity of the NH and OH stretchings at 3305 cm⁻¹ increased with time. However, both the catalyzed and uncatalyzed polymerizations failed to convert all the carbonate linkages into the urethane linkages unlike the small molecule model reaction (Fig. 4) due to the restriction in chain mobility with increasing conversion.

Figure 7 shows the FTIR spectra of PHU-2 and PHU-3. In PHU-2 and PHU-3, the C=O stretching of the carbamates overlaps with the carbonyl group of the ester. There is a broad peak at 3361 cm⁻¹ for the NH and OH stretchings of the carbamate linkage for PHU-2 and PHU-3, and additional peaks for the carbamate linkage appear at 1238 and 1527 cm⁻¹ for the N-H bending and C-N stretching. From the FTIR analyses, it appears that there are residual cyclic carbon-

ate linkages (~1790 cm⁻¹) present in these polymers after 24 h. On the basis of a total equimolar mixture of amine and carbonate functional groups, the theoretical gelation point p_c ($p_c = 2/f_{avg}$, where p_c is the critical extent of reaction at the gel point and f_{avg} is the average functionality of the polymerization system) for the polymerization of DETA with Bis-CC, Tris-CC, and Tetra-CC occurs at 82%, 67%, and 58% conversions, respectively. Thus, the gelation point of the polymerization is reached at lower conversion as functionality increases. The conversion was qualitatively monitored using the intensity of the carbonyl stretching for the carbonate moiety in the FTIR spectra. We determined that the conversion of the polymerization reaction for Tris-CC and DETA was greater than that for the polymerization of Tetra-CC and DETA (see Fig. 7). This result followed the theoretical prediction.

As a concrete demonstration of the robust and facile nature of the polyaddition, we added equimolar mixtures of a multifunctional cyclic carbonate and DETA to a Teflon dish and placed these mixtures in an oven at 80 $^{\circ}$ C for 24 h to produce the PHUs. The multi-functional cyclic carbonates were



FIGURE 6 FTIR spectra of DOU (top), PHU-1 (middle), and PHU-4a (bottom).

immediately used after the thiol-ene reaction without purification of unreacted starting material and initiator. Figure 8 shows photos of the resulting polymers after the polymerization. We are not concerned about the tendency of the monomeric reagent to limit the molecular weight of the polymer formed since it will be a crosslinked material. The robustness of the ringopening polyaddition of amine to carbonate eliminates the need for purification prior to polymerization. Hence, the simplicity of this reaction allows for easy scale-up in an industrial setting.

To tune the chemical and thermal properties of the poly(hydroxyl urethane)s, Bis-CC and 1,6-diaminohexane were polymerized with various contents of DETA to produce PHU-4 (Scheme 4). This polymerization provided an opportunity to compare PHU-1 with PHU-4 and to access different materials for thermal analyses. PHU-4a and PHU-4b were generated using 10 and 24 mol % DETA, respectively, relative to the mole of Bis-CC. The conversion of the cyclic carbonate was quantitative in the polymerization of Bis-CC, 1,6-diaminohexane, and 10 mol % DETA (relative to the mole of cyclic carbonate) at 80 °C for 24 h in the absence of a catalyst. Using 24 mol % DETA in the polymerization, we found that full conversion was hindered by a lower value for the theoretical gelation point (94% conversion for this system vs. 98% conversion for the former). Figure 6 shows the FTIR spectrum of the resulting polymer PHU-4a, which is compared to those



FIGURE 7 FTIR spectra of PHU-2 (top) and PHU-3 (bottom).



FIGURE 8 Pictures of crosslinked poly(hydroxyl urethane) produced from Bis-CC, Tris-CC, and Tetra-CC with DETA.

of DOU and PHU-1. The profiles of the three spectra are similar, except for the presence of a v(C=0) vibration of the cyclic carbonate (1794 cm⁻¹) in PHU-1.

Thermal Analysis

Table 1 summarizes the glass transition temperatures (T_g) and thermal decomposition temperatures (T_d), which were determined as the 5% mass loss, of different PHUs. From the DSC analysis, PHU-1s have T_g between 3 and 12 °C. The T_g of PHUs produced with and without a catalyst (polymerization time = 72 h) are similar. PHU-2 and PHU-3 have similar T_g



SCHEME 4 Synthesis of CO_2 -based, crosslinked poly(hydroxyl urethane) using bis(cyclic carbonate), 1,6-diaminohexane, and diethylenetriamine.

TABLE 1 Decomposition Temperatures (T_d) of Poly(hydroxyl urethane)s^a

<i>Т</i> _d ^b (°С)	<i>T</i> _g (°C
-	3
190	11
217	5
208	12
193	16
186	16
230	-1
231	7
	T _d ^b (°C) - 190 217 208 193 186 230 231

 $^{\rm a}$ Polymerization was conducted at 80 $^{\circ}{\rm C}$ for 24 h without catalyst unless noted otherwise.

^b Determined as 5% mass loss.

^c Polymerization was conducted at room temperature.

^d Used LiBr as a catalyst and polymerization time 48 h.

^e Polymerization time 72 h.

even though the functionality of these cyclic carbonates is different. Furthermore, the $T_{\rm g}$ of poly(hydroxyl urethane)s produced from Bis-CC, 1,6-diaminohexane, and DETA ranges from -1 to 7 °C. Most PHUs are used in hydrogel or coating applications,¹⁵ but these materials exhibit good adhesive properties and are candidate materials for adhesive applications.

The thermal stability of these polymers was measured with a thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The $T_{\rm d}$ of PHU-1 (190 °C), produced using LiBr as a catalyst, is lower than that of the uncatalyzed system (217 °C). Both samples were analyzed twice; the result was consistent with the observation above. This result indicates that the catalyst accelerates the decomposition, probably thru nucleophilic attack of the polymer backbone. The polymerization of Bis-CC and DETA was allowed to proceed for 24 and 72 h; however, the longer polymerization time did not yield a more thermally stable polymers. Under the same polymerization conditions, the thermogravimetric results showed that PHU-1 (217 °C) has higher thermal stability than PHU-2 (193 °C) and PHU-3 (186 °C). This trend indicates that the thermal stability of these crosslinked PHUs decreases due to increasing density of C-S bond and qualitatively lower conversion is observed with increasing functionality. PHU-4s have the highest $T_{\rm d}$ (230 °C) of the polymers synthesized in this study, and the thermal stability of this system seems to be independent of the quantity of crosslinker.

Endo et al.¹⁹ have reported that non-crosslinked poly-(hydroxyl urethane)s, produced from terephthalic acid bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester and H₂N-(CH₂)_n-NH₂ (n = 2 - 6), have T_{d} s between 177 and 208 °C. From the perspective of bond types, the difference between their and our polymers (PHU-2 and PHU-3) is the lack of C—S bond in their polymers. The thermal stability of non-crosslinked and crosslinked PHUs is similar.

CONCLUSIONS

We have presented the synthesis of CO_2 -based, crosslinked poly(hydroxyl urethane)s via a set of robust, atomically efficient, and facile reactions. First, the thiol-ene reaction between VEC and different thiols produced multi-functional cyclic carbonates (i.e., Bis-CC, Tris-CC, and Tetra-CC) in quantitative yield. The polyaddition of DETA (and 1,6-diaminohexane in some cases) with the multi-functional cyclic carbonates provided an easy and effective technique for producing polymeric materials with tunable properties. The thermal properties of the crosslinked polymers were characterized by DSC and TGA. PHU-2 and PHU-3 have the highest $T_{\rm g}$ whereas PHU-4 showed the best thermal stability. From the physical and thermal properties, these materials are potential candidates in adhesive and sealant applications. Overall, we showed a simple method to incorporate CO₂ into polymer via the use of cyclic carbonate chemistry.

This work was funded and supported by U.S. Department of Energy's Office of Fossil Energy. The authors thank Dr. Sheila Hedges and Dr. Jeffrey Culp for the training and use of differential scanning calorimeter and thermogravimetric analyzers.

REFERENCE AND NOTES

1 Haszeldine, R. S. Science 2009, 325, 1647-1652.

2 Melillo, J. M.; McGuire, A. D.; Kicklighter, D. W.; Moore, B.; Vorosmarty, C. J.; Schloss, A. L. Nature 1993, 363, 234–240.

3 Sarmiento, J. L.; Le Quéré, C. Science 1996, 274, 1346-1350.

4 Hansen, J.; Johnson, D.; Lacis, A.; Lebedeff, S.; Lee, P.; Rind, D.; Russell, G. Science 1981, 213, 957–966.

5 Song, C. Catal Today 2006, 115, 2–32.

6 Kihara, N.; Endo, T. J Polym Sci Part A: Polym Chem 1993, 31, 2765–2773.

7 Tomita, H.; Sanda, F.; Endo, T. J Polym Sci Part A: Polym Chem 2001, 39, 860–867.

8 Webster, D. Prog Org Coat 2003, 47, 77.

9 Allen, S. D.; Byrne, C. M.; Coates, G. W. In Feedstocks for the Future;Bozell, J. J.; Patel, M. K., Eds.; ACS Symposium Series 921; American Chemical Society: Washington, DC, 2006; pp 116–129.

10 Darensbourg, D. J Chem Rev 2007, 107, 2388-2410.

11 Belliveau, B. P.; Downie, R. B. U.S. Patent 7,588,707, September 15, 2009.

12 Zhu, Z.; Einset, A. G.; Yang, C.-Y.; Chen, W.-X.; Wnek, G. E. Macromolecules 1994, 27, 4076–4079.

13 Sakakura, T.; Choi, J.-C.; Yasuda, H. Chem Rev 2007, 107, 2365–2387.

14 Vora, A.; Nasrullah, M.; Webster, D. J Coat Technol Res 2010, 7, 409–417.

15 Anderson, A. G. U.S. Patent 5,977,262, November 2, 1999.

16 December, T. S.; Harris, P. J. U.S. Patent 5,431,791, July 11, 1995.

17 Frishchinger, I.; Cotting, J.; Finter, J.; Francois, J. U.S. Patent 6,090,891, July 18, 2000.

18 Pacheco, M. A.; Marshall, C. L. Energy Fuels 1997, 11, 2–29.

19 Steblyanko, A.; Choi, W.; Sanda, F.; Endo, T. J Polym Sci Part A: Polym Chem 2000, 38, 2375–2380.

20 Shaikh, A.-A. G.; Sivaram, S. Chem Rev 1996, 96, 951-976.

21 Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. Chem Commun 2011, 47, 212–214.

22 North, M.; Pasquale, R.; Young, C. Green Chem 2010, 12, 1514–1539.

23 Darensbourg, D. J.; Horn, A., Jr.; Moncada, A. I. Green Chem 2010, 12, 1376–1379.

24 Ji, D.; Lu, X.; He, R. Appl Catal A: Gen 2000, 203, 329-333.

25 Rokicki, G.; Rakoczy, P.; Parzuchowski, P.; Sobiecki, M. Green Chem 2005, 7, 529–539.

26 Aresta, M.; Dibenedetto, A. J Mol Catal A: Chem 2002, 182–183,399–409.

27 Eghbali, N.; Li, C.-J. Green Chem 2007, 9, 213-215.

28 Huang, S.; Liu, S.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. J Fuel Chem Technol 2007, 35, 701–705.

29 Decortes, A.; Martinez Belmonte, M.; Benet-Buchholz, J.; Kleij, A. W. Chem Commun 2010, 46, 4580–4582.

30 Paddock, R. L.; Nguyen, S. T. J Am Chem Soc 2001, 123, 11498–11499.

31 Trost, B. M.; Angle, S. R. J Am Chem Soc 1985, 107, 6123–6124.

32 Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.-i.; Sakai, S. Chem Lett 1985, 14, 199–200.

33 Bai, D.; Jing, H.; Liu, Q.; Zhu, Q.; Zhao, X. Catal Commun 2009, 11, 155–157.

34 Bai, D.; Jing, H. Green Chem 2010, 12, 39-41.

35 Xiong, Y.; Wang, H.; Wang, R.; Yan, Y.; Zheng, B.; Wang, Y. Chem Commun 2010, 46, 3399–3401.

36 Paddock, R. L.; Nguyen, S. T. Chem Commun 2004, 1622–1623.

37 Jing, H.; Nguyen, S. T. J Mol Catal A: Chem 2007, 261, 12–15.

38 Sun, J.; Wang, L.; Zhang, S.; Li, Z.; Zhang, X.; Dai, W.; Mori, R. J Mol Catal A: Chem 2006, 256, 295–300.

39 Li, F.; Xiao, L.; Xia, C.; Hu, B. Tetrahedron Lett 2004, 45, 8307–8310.

40 Barkakaty, B.; Morino, K.; Sudo, A.; Endo, T. Green Chem 2010, 12, 42–44.

41 Wang, J.-L.; Wang, J.-Q.; He, L.-N.; Dou, X.-Y.; Wu, F. Green Chem 2008, 10, 1218–1223.

42 Gesser, H. D.; Lafreniere, D. R. T. Prog Org Coat 2004, 49, 372–374.

43 Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H.; Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. Green Chem 2003, 5, 497–507.

44 Takizawa, K.; Nulwala, H.; Thibault, R. J.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K. L.; Hawker, C. J. J Polym Sci Part A: Polym Chem 2008, 46, 2897–2912.

45 Nulwala, H.; Burke, D. J.; Khan, A.; Serrano, A.; Hawker, C. J. Macromolecules 2010, 43, 5474–5477.

46 Nulwala, H.; Takizawa, K.; Odukale, A.; Khan, A.; Thibault, R. J.; Taft, B. R.; Lipshutz, B. H.; Hawker, C. J. Macromolecules 2009, 42, 6068–6074.

47 Campos, L. M.; Truong, T. T.; Shim, D. E.; Dimitriou, M. D.; Shir, D.; Meinel, I.; Gerbec, J. A.; Hahn, H. T.; Rogers, J. A.; Hawker, C. J Chem Mater 2009, 21, 5319–5326.

48 Campos, L. M.; Meinel, I.; Guino, R. G.; Schierhorn, M.; Gupta, N.; Stucky, G. D.; Hawker, C. J. Adv Mater 2008, 20, 3728–3733.

49 Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. Macromolecules 2008, 41, 7063–7070.

50 Killops, K. L.; Campos, L. M.; Hawker, C. J. J Am Chem Soc 2008, 130, 5062–5064.

51 Montanez, M. I.; Campos, L. M.; Antoni, P.; Hed, Y.; Walter, M. V.; Krull, B. T.; Khan, A.; Hult, A.; Hawker, C. J.; Malkoch, M. Macromolecules 2010, 43, 6004–6013.

52 Hagberg, E. C.; Malkoch, M.; Ling, Y.; Hawker, C. J.; Carter, K. R. Nano Lett 2007, 7, 233–237.

53 Antoni, P.; Robb, M. J.; Campos, L.; Montanez, M.; Hult, A.; Malmström, E.; Malkoch, M.; Hawker, C. J Macromolecules 2010, 43, 6625–6631.

54 Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J Chem Rev 2009, 109, 5620–5686.

55 Joralemon, M. J.; O'Reilly, R. K.; Hawker, C. J.; Wooley, K. L. J Am Chem Soc 2005, 127, 16892–16899.

56 Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. J Am Chem Soc 2005, 127, 14942–14949.

57 O'Reilly, R. K.; Joralemon, M. J.; Wooley, K. L.; Hawker, C. J. Chem Mater 2005, 17, 5976–5988.

58 Thibault, R. J.; Takizawa, K.; Lowenheilm, P.; Helms, B.; Mynar, J. L.; Fréchet, J. M. J.; Hawker, C. J. J Am Chem Soc 2006, 128, 12084–12085.

59 Hein, J. E.; Tripp, J. C.; Krasnova, L. B.; Sharpless, K. B.; Fokin, V. V. Angew Chem Int Ed 2009, 48, 8018–8021.

60 Díaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. J Polym Sci Part A: Polym Chem 2004, 42, 4392–4403.

61 Hawker, C. J.; Wooley, K. L. Science 2005, 309, 1200–1205.

62 Malkoch, M.; Vestberg, R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A. F.; Hedrick, J. L.; Liao, Q.; Frank, C. W.; Kingsbury, K.; Hawker, C. J. Chem Commun 2006, 2774–2776.

63 van Berkel, K. Y.; Hawker, C. J. J Polym Sci Part A: Polym Chem 2010, 48, 1594–1606.

64 Kade, M. J.; Burke, D. J.; Hawker, C. J. J Polym Sci Part A: Polym Chem 2010, 48, 743–750.

65 Boyer, C.; Granville, A.; Davis, T. P.; Bulmus, V. J Polym Sci Part A: Polym Chem 2009, 47, 3773–3794.

66 Yu, B.; Chan, J. W.; Hoyle, C. E.; Lowe, A. B. J Polym Sci Part A: Polym Chem 2009, 47, 3544–3557.

67 Van Holen, J. U.S. Patent 0,113,594 A1, May 26, 2005.

68 Tomita, H.; Sanda, F.; Endo, T. J Polym Sci Part A: Polym Chem 2001, 39, 3678–3685.

69 Rousseau, J.; Rousseau, C.; Lynikaite, B.; Sackus, A.; de Leon, C.; Rollin, P.; Tatibouët, A. Tetrahedron 2009, 65, 8571–8581.