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Facile Room-Temperature Preparation of Flexible Polyurethane Foams from Carbon Dioxide Based Poly(ether carbonate) Polyols with a Reduced Generation of Acetaldehyde

Jeong Hyeon Jang,[†] Jae Hee Ha,[‡] Il Kim,*[,§] Joon Hyun Baik,*[,‡] and Sung Chul Hong*[,†]

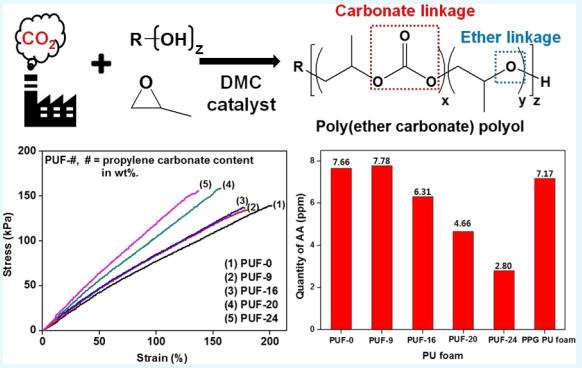
[†]Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Republic of Korea

[‡]Energy Research Group, Research Institute of Industrial Science & Technology (RIST), Pohang 37673, Republic of Korea

[§]Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

Supporting Information

ABSTRACT: Carbon dioxide (CO_2) is becoming more attractive as a renewable feedstock for chemical synthesis. In this study, CO_2 was incorporated into poly(ether carbonate) (PEC) polyols by using a double-metal-cyanide catalyst. By adjusting the CO_2 pressure, the content of propylene carbonate units in the PEC polyols was controlled, indicating successful and semiquantitative incorporation of CO_2 into the PEC polyols. Polyurethane foams (PUFs) with different propylene carbonate content were easily prepared at room temperature by employing the PEC polyols due to their adequate viscosity under ambient conditions. The firmness of the PUFs increased as the amount of propylene carbonate units increased due to the rigidity of the carbonate linkage, representing predictable mechanical properties. Interestingly, reduced generation of volatile organic compounds (VOCs) from the PUFs, namely acetaldehyde, was observed with a high content of propylene carbonate units at 120 °C, indicating good stability of the carbonate units against thermo-oxidative decomposition. This study demonstrates the importance of CO_2 as an environmental-friendly and renewable resource that can provide not only industrially important but also problem-solving products in terms of processability and low generation of VOCs.



INTRODUCTION

Carbon dioxide (CO_2) is a highly attractive renewable resource due to its abundant, inexpensive, and nontoxic nature. Various approaches for chemical fixation of CO_2 have been attempted to address the growing concern of global warming.[1−5] The utilization of CO_2 as a starting material to prepare industrially important polymers is particularly interesting and not only contributes to the reduction of greenhouse gas but also provides a value-added product.[6−9] In this regard, the preparation of polyols from CO_2 has been an interesting topic for chemists and chemical engineers.[7,10−12]

Polyols are an important raw material for the production of polyurethane (PU) and can be classified into three different types: polyester, polyether, and polycarbonate (PC).[13] Essentially, the production of polyols from CO_2 leads to the copolymerization between CO_2 and epoxides due to its low energy level.[3,12] Through this copolymerization, CO_2 is incorporated into polyols as a carbonate unit.[14,15] Depending on the catalyst, this copolymerization produces two different types of copolymers with different compositions: PC polyol or poly(ether carbonate) (PEC) polyol (Scheme 1a). The use of selected Lewis acid catalysts produces PC polyols with improved biodegradability and anticorrosion properties.[11,16,17] However, the use of the PC polyol as a raw material to prepare PUs is not easy because of its high glass transition temperature (T_g) and high viscosity at room temperature.[7,17]

CO_2-based PEC polyols, containing both carbonate and ether linkages in their chemical structure, can be prepared by using a double-metal-cyanide (DMC) catalyst (Scheme 1b).[7,18,19] DMC catalysts, such as zinc−cobalt and zinc−nickel DMC catalysts, have been demonstrated as efficient catalysts for ring-opening polymerization of epoxides and CO_2.[8,9,20−23] CO_2-based PEC polyols from the DMC catalysts exhibited a narrow polydispersity index and better flexibility than PC polyols due to the ether linkage in their chemical structure.[24] A life cycle assessment study of the CO_2-based PEC polyols suggested a reduction of greenhouse gases by 11−19% compared with that of conventional polyether polyols.[18] In addition, the PEC polyols exhibit better hydrolysis resistance and oxidative stability compared with polyester- and polyether-type polyols.[19] Chemical and oxidative stability derived from PEC polyols are important and highly desirable properties in PU applications. Therefore, the PEC polyols represent

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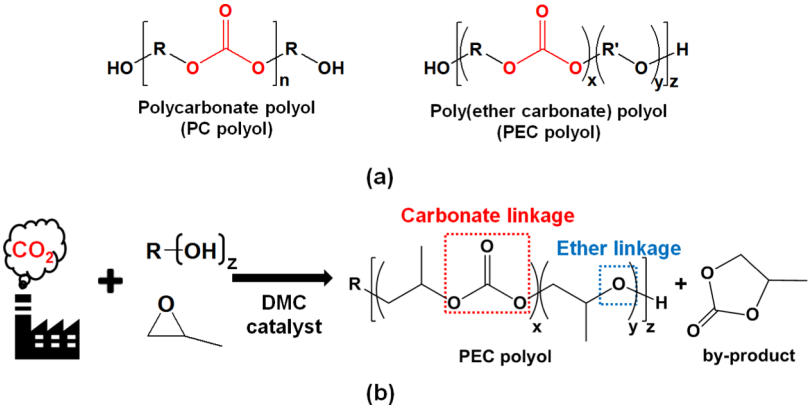
Scheme 1. Representative Chemical Structure of PC and PEC Polyols (a) and Copolymerization of CO_2 and propylene oxide (PO) by Double-Metal-Cyanide (DMC) Catalyst in the Presence of Polyhydric Alcohol Initiator to Afford PEC Polyols (b)



substitutable and sustainable polyols, which exemplify the chemical conversion of renewable CO_2 into valuable products.

PU is an important polymer that is used in various forms, such as foams, coatings, elastomers, and adhesives, to name a few.[13,25] Owing to its versatility, PU has been used in a wide range of applications, including automotive seats, furniture, thermal insulators, packaging materials, and medical devices. Flexible PU foam (PUF) is an interesting type of PU because of its large number of uses. Flexible PUF is prepared by the reaction between isocyanates and polyols, where the characteristics of polyols considerably affect the final properties of PUs. Thus, an in-depth study needs to be carried out to clarify the correlation between the properties of the raw materials and the properties of the resulting PUs.

Recently, a number of attempts to utilize CO_2-based polyols for the preparation of PUs have been reported. Langanke et al. reported an initial application of PEC polyols for PUFs.[7] DeBolt et al. prepared flexible PUFs with a mixture of conventional polyether polyols and CO_2-based PC polyols.[17] Wang et al. reported waterborne PUs with PEC polyols exhibiting improved hydrolysis and oxidation resistance.[19] Orgilés-Calpena et al. reported a PU adhesive from a mixture of polyester and PC polyols for footwear.[26] We also reported thermoplastic PUs from a mixture of polyether and PC polyols for coatings with improved anticorrosion properties.[11] However, most studies adopted a mixture of CO_2-based polyols and conventional polyols, mainly due to the aforementioned high viscosity and poor processability of the PC polyol. Therefore, the development of CO_2-based PEC polyols with inherently improved processability for easy preparation of PUFs is desired.

In this study, both ether and carbonate units were incorporated into one polyol molecule, providing the liquid PEC polyols with a sufficiently low viscosity at room temperature. Control of the amount of propylene carbonate units in the PEC polyols was attempted by adjusting the CO_2 pressure to examine the effect of different ether/carbonate compositions on its characteristics. The effect of propylene carbonate content on the characteristics of the resulting PUFs was also studied, including their volatile organic compound (VOC) emission behaviors. A quantitative analytical tool developed by our group was adopted to assess the VOC issue by using a headspace-gas chromatography-flame ionization detector (HS-GC−FID) system.[27]

EXPERIMENTAL SECTION

Materials. 2-Ethoxyethyl acetate (EEA, 98%), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123, M_n ∼ 5800 g/mol), zinc chloride ($ZnCl_2$, >98%), and potassium hexacyanocobaltate (III) ($K_3[CO(CN)_6]$, >97%) were obtained from Aldrich (St. Louis, MO) and used as received. Propylene oxide (PO, 99%, Samchun Chemicals, Pyeongtaek, Korea), glycerol propoxylate (M_n ∼ 1000 g/mol, OH functionality = 3, PPG-1000 grade from Kumho Petrochemical, Seoul, Korea), and CO_2 (99.999%, Korea Gas Technology, Sangju, Korea) were used as received. Tin(II) 2-ethylhexanoate (T-9, Air Products, Allentown, PA), DABCO 33-LV (solution of 33% triethylenediamine and 67% dipropylene glycol, Air Products, Allentown, PA), Niax silicone (L-580, Momentive Performance Materials Inc., Waterford, NY), polypropylene glycol (PPG, M_n ∼ 2000 g/mol, Sigma-Aldrich, St. Louis, MO), poly(hexamethylene carbonate) diol (UH-200, M_n ∼ 2000 g/mol, UBE, Ube, Japan), poly(propylene carbonate) diol (Converge Polyol 212-20, M_n ∼ 2000 g/mol, Saudi Aramco, Dhahran, Saudi Arabia), and a dibasic ester mixture (DBE, Sigma-Aldrich, St. Louis, MO) were also used without further purification. Toluene 2,4-diisocyanate (TDI, >98%) was purchased from Daejung Chemicals (Siheung, Korea) and stored under nitrogen. All other chemicals were used without specific purification.

Preparation of DMC Catalyst. The DMC catalyst was prepared by using EEA and P123 as complexing and co-complexing agents, respectively. The solution with $ZnCl_2$ (12 g, 88 mmol) and EEA (15 mL, 111 mmol) in water (46 mL) was stirred for 10 min at 50 °C. $K_3[Co(CN)_6]$ solution containing 1.3 g of $K_3[Co(CN)_6]$ (3.91 mmol) in 16 mL of water was added to this solution and stirred for 1 h. The solution of complexing agents, composed of EEA (13.5 mL, 97.0 mmol) and P123 (0.97 g, 0.167 mmol), was mixed with the former solution and stirred for an additional 3 min. The precipitate was collected through centrifugation and washed with a solution of complexing agents, composed of EEA (6.75 mL, 49.8 mmol) and P123 (0.485 g, 0.084 mmol), at least three times, followed by drying under vacuum at 80 °C overnight.

Preparation of PEC Polyols. PEC polyols were synthesized with the DMC catalyst in a high-pressure reactor (Model No. 4568, Parr Instrument Company, Figure S1, see the Supporting Information). A series of PEC polyols with different propylene carbonate contents were prepared under

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five different CO_2 pressures, namely, 0, 5, 10, 15, and 20 bar (Table 1). Glycerol propoxylate was used as an initiator for preparing PEC polyols. The typical polymerization procedure was as follows. A quantity of 0.225 g of DMC catalyst was introduced into the reactor, followed by pressurizing with CO_2 to the desired pressure. After heating the reactor to 115 °C, PO (90 mL, 77.31 g) and 30 mL of glycerol propoxylate were fed into the reactor for 90 min by using an HPLC pump. The polymerization was stopped after an additional reaction for 30 min. All PEC polyols were washed through extraction with distilled water to remove cyclic propylene carbonate (CPC) byproduct.

Preparation of PUFs with PEC Polyols. PUFs with five different PEC polyols were prepared following a two-step procedure (Scheme 2 and Table 2). The representative procedure to prepare the PUFs is as follows. First, the polyol, tin catalyst (T-9), amine catalysts (DABCO 33-LV), silicone surfactant (L-580), and distilled water were stirred in a bath equipped with an overhead stirrer at 2000 rpm for 3 min (component A). Then, TDI as component B was added to component A, followed by further stirring at 2000 rpm for 10 s. The reaction mixture was quickly poured into an open mold (9.0 cm × 19.0 cm × 8.5 cm) to allow free rising of the foam. After the foam rising was complete, the foam was thermally aged in an oven at 110 °C for 5 min. The resulting PUF was then kept at room temperature for approximately 24 h for stabilization. The isocyanate index (NCO index, [NCO]/[OH]) was kept constant at 1.1 for all PUFs. Each PUF was prepared at least three times to confirm the reproducibility of the process.

Characterization. Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 500 MHz Avance to elucidate the structural characteristics of the PEC polyols. The ^{1}H NMR spectra were obtained at room temperature using deuterated chloroform as a solvent. The weight and molar fraction of propylene carbonate units (W_c and F_c, respectively) in the polymer chain was determined by the area values of the ^{1}H NMR signals following eqs 1 and 2, respectively[23]

$$W_c = \frac{102A_{1.3}}{58A_{1.15} + 102A_{1.3}} \quad (1)$$

$$F_c = \frac{A_{1.3}}{A_{1.15} + A_{1.3}} \quad (2)$$

where $A_{1.15}$ and $A_{1.3}$ are the area values of ^{1}H NMR signals at 1.15 and 1.3 ppm, respectively. Size-exclusion chromatography (SEC) was performed on a Shimadzu LC-20A equipped with PSS columns (Styragel HR 2, 4, and 5) and a Shimadzu RID-10A refractive index detector. Tetrahydrofuran (HPLC grade) was used as an eluent at a flow rate of 1.0 mL/min. The calibration curve was obtained using a polystyrene standard. Matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS) spectra were obtained on a Voyager mass spectrometer (Applied Biosystems). Volumetric titrations to determine the hydroxyl values of the polyols were performed according to ASTM D1957-86. The hydroxyl value refers to the weight (in mg) of potassium hydroxide required to titrate the free acetic acid generated during the acetylation of hydroxyl groups. The hydroxyl value (mg-KOH/g) was calculated using the following eq 3 (ASTM D1957-86)

Table 1. Preparation and Characteristics of CO_2-Based PEC Polyols[a]

designation of polyol	CO_2 pressure (bar)	polyol product (g)	CPC by-product[b] (g)	productivity (g-polyol/g-catalyst)	conversion of PO (%)	W_c[c] (wt %)	F_c[d] (mol %)	$M_{n,Maldi}$[e] (g/mol)	$M_{n,SEC}$[f] (g/mol)	PDI[f]	hydroxyl value[g] (mg-KOH/g)	average OH functionality[h]	viscosity[i] (cps)
PEC polyol-0	0	107.80	0	479.11	99.96			2117	3370	1.11	73	2.75	582
PEC polyol-9	5	97.13	9.84	431.69	88.46	9.39	5.56	2060	3110	1.12	68	2.50	974
PEC polyol-16	10	93.53	23.90	415.69	90.97	16.03	9.79	1932	2970	1.19	70	2.41	1840
PEC polyol-20	15	82.22	36.68	365.42	85.21	19.51	12.12	1624	2740	1.24	79	2.29	2856
PEC polyol-24	20	72.38	44.16	321.69	77.20	24.29	15.43	1388	2570	1.21	85	2.10	3082

[a]Preparation conditions: PO, 77.31 g; DMC, 0.225 g; glycerol propoxylate, 30 mL; temperature, 115 °C; time, 2 h. [b]Cyclic propylene carbonate byproduct. [c]Weight fraction of propylene carbonate units (W_c) in polyol calculated by eq 1. [d]Molar fraction of propylene carbonate units (F_c) in polyol calculated by eq 2. [e]Number average molecular weight determined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). [f]Number average molecular weight and polydispersity index (M_w/M_n) values determined by size-exclusion chromatography (SEC) analyses: M_w, weight average molecular weight. [g]Determined by titration method following ASTM D1957-86. [h]Average number of OH functionality per molecule = (hydroxyl value × $M_{n,Maldi}$)/56 100. [i]At 25 °C.

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Scheme 2. Schematic Representation of the Preparation of PUFs Employing the PEC Polyol in This Study

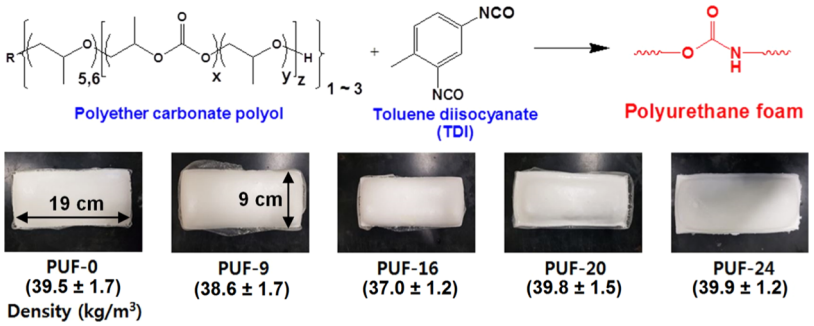

Table 2. Formulations to Prepare Flexible Polyurethane Foam (in pphp, Part per Hundred Parts Polyol by Weight)[a]

formulation	PUF-0	PUF-9	PUF-16	PUF-20	PUF-24
polyol	PEC polyol-0	PEC polyol-9	PEC polyol-16	PEC polyol-20	PEC polyol-24
	100	100	100	100	100
T-9	0.20	0.20	0.20	0.10	0.05
DABCO-33LV	0.40	0.40	0.40	0.40	0.40
L580	1.00	1.00	1.00	1.00	1.00
water	3.0	3.0	3.0	3.0	3.0
TDI	44.22	43.56	43.92	45.48	46.48

[a]NCO index, [NCO]/[OH] = 1.10.

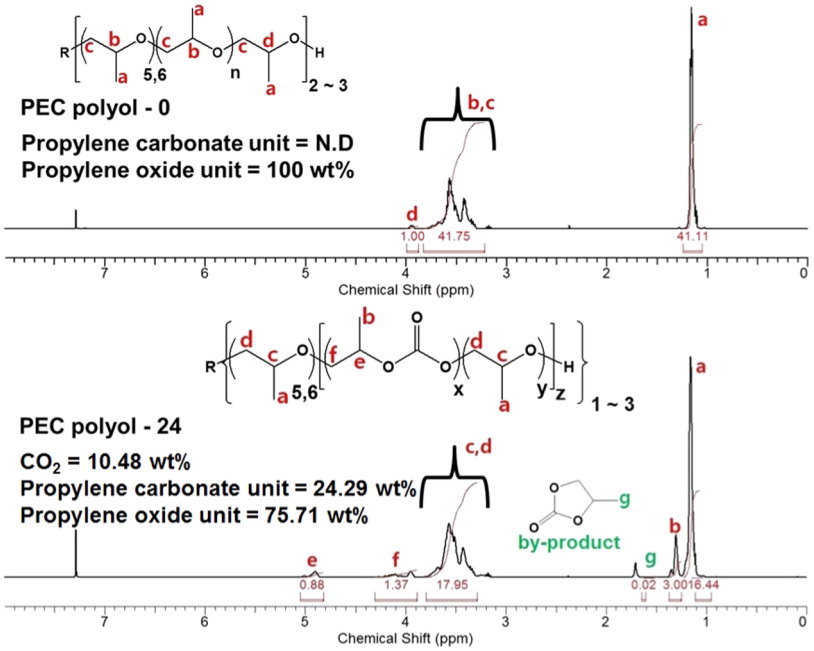

Figure 1. Representative ^{1}H NMR spectra of PEC polyols: PEC polyol-0 and -24.

$$\text{hydroxylvalue} = \frac{(A - B) \times N \times 56.1}{S} \quad (3)$$

where A, B, N, and S are the volume (in mL) of the potassium hydroxide solution used for the blank test (without the sample), the volume (in mL) of the potassium hydroxide solution used for the titration of the sample, the molar concentration of the potassium hydroxide solution, and the weight (in g) of the sample, respectively. The viscosity of PEC polyols was measured on a Brookfield DV3T Rheometer at 25 °C and 60 rpm. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 FT-IR spectrometer at a resolution of 4 cm^{-1} over a wavenumber range of 4000−650 cm^{-1}. Thermogravimetric analyses (TGA) were performed on a TGA4000 (PerkinElmer). The samples (7−10 mg) were heated from room temperature to 800 °C under a nitrogen flow of 20 mL/min at a heating rate of 10 °C/min. The core density of the PUF samples was determined according to ASTM standard D3574-03. Four samples per foam formulation were measured, and the average result was reported. The mechanical properties of the PUFs were investigated by subjecting dumbbell-shaped specimens to tensile tests. The tensile tests were performed using a universal testing machine (AGS-5kNX, Shimadzu) at room temperature following ASTM standard D3574-03. The results from at least three samples were averaged to determine the mechanical property

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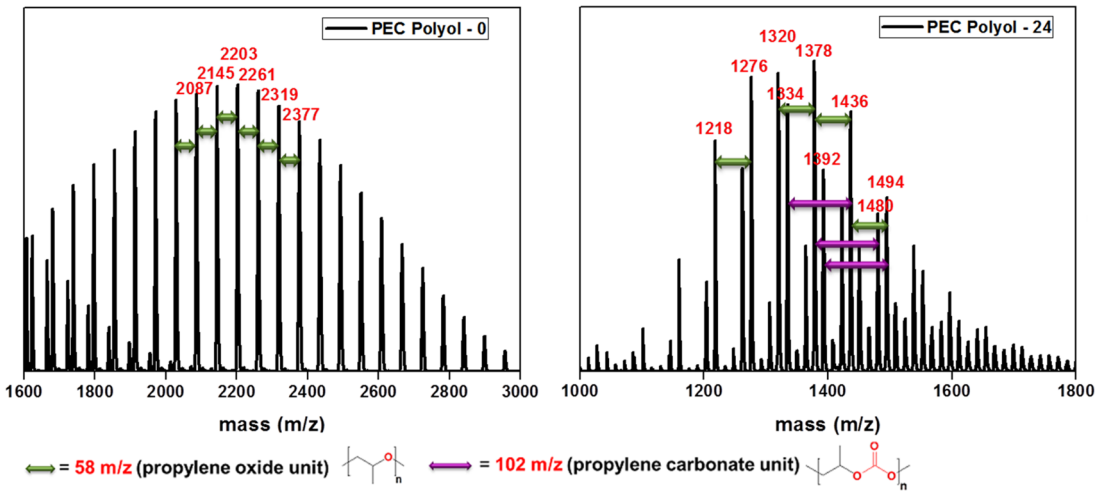

Figure 2. Representative MALDI-TOF MS spectra of PEC polyols: PEC polyol-0 and -24.

values. Detailed experimental procedures to determine the amount of acetaldehyde (AA) by using HS-GC−FID are described in our previous report.[27] A Shimadzu GC-2010 instrument equipped with a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm, Agilent) and FID was employed for the GC experiments. The HS thermal treatment was conducted at 120 °C for 20 min by using a manual HS machine from Netel India Ltd.

RESULTS AND DISCUSSION

CO_2-based PEC polyols were prepared by using DMC catalyst with EEA as a complexing agent. The DMC−EEA catalyst efficiently provided bifunctional PEC polyol with high yield, as evidenced by the average OH functionality values (2.10−2.75, Table 1) and the high conversion of PO (77.20−99.96%, Table 1).[28] The DMC−EEA catalyst also incorporated CO_2 into PEC polyols efficiently, as confirmed by relatively high W_c values from ^{1}H NMR investigations (Table 1 and Figure 1).

The signals of ^{1}H NMR at 1.1−1.2 ppm represent protons in the CH_3 groups in propylene ether units (Figure 1). The negligible intensity of the signal g at 1.6 ppm (protons of the CH_3 group in CPC as a byproduct) of PEC polyol-24 in Figure 1 demonstrated favored incorporation of CO_2 into polyol chains (relatively low amounts of CPC byproducts versus polyol products in Table 1) and efficient removal of the byproduct by washing procedure with water (Figure S2, see the Supporting Information).[23,29] During this washing procedure, the DMC catalyst was also believed to be removed through decomposition. Signals at 4.8−5.0, 3.9−4.3, and 1.3−1.5 ppm of PEC polyol-24 in Figure 1 were assigned to CH, CH_2, and CH_3 groups in propylene carbonate units, respectively. Obviously, the intensities of these signals increased with higher CO_2 pressure during the preparation of PEC polyols (Figure S3, see the Supporting Information). The PEC polyols exhibited W_c values of 0, 9.39, 16.03, 19.51, and 24.29 wt % for PEC polyol-0, -9, -16, -20, and -24, respectively. The results suggested a controlled incorporation of CO_2 into the PEC polyol chains simply by adjusting the CO_2 pressure during copolymerization. It should also be noted that the decreased amount of polyols (the amount of polyol product and the productivity values in Table 1) and more amount of CPC byproducts (CPC by-product values in Table 1) were obtained with higher pressure of CO_2, likely due to decreased stability of zinc-carboxylate intermediates against back-biting decomposition reaction of the DMC catalyst.[29]

The incorporation of CO_2 into polyols as propylene carbonate units was also confirmed by a molecular weight investigation (Figures 2 and S4, see the Supporting Information). MALDI-TOF MS spectra of the polyether polyol (e.g., PEC polyol-0 in Figure 2) and PEC polyol (e.g., PEC polyol-24 in Figure 2) exhibited molecular weight differences between the peaks of 58 g/mol (green arrows), representing the presence of propylene ether units. At the same time, PEC polyols prepared under pressurized CO_2 (PEC polyol-24 in Figure 2 and PEC polyol 9, 16, 20, and 24 in Figure S4, see the Supporting Information) additionally exhibited molecular weight difference between the peaks of 102 g/mol (purple arrows). The molecular weight difference of 102 g/mol clearly represented the presence of propylene carbonate units. The exact molecular weight values of the PEC polyols ($M_{n,Maldi}$ in Table 1) determined from the MALDI-TOF MS spectra decreased with increased CO_2 pressure, also suggesting a retarded propagation reaction of the DMC catalyst in the presence of CO_2.[29] The decreased molecular weight values of the PEC polyols with higher CO_2 pressure were also confirmed by SEC analyses (Table 1). The number average molecular weight values of the PEC polyols determined by SEC analyses ($M_{n,SEC}$) were slightly higher than the corresponding $M_{n,Maldi}$ values, likely due to the different hydrodynamic volumes of the polystyrene standards employed for SEC analyses.

To determine the hydroxyl value of PEC polyols, a titration method (ASTM D1957-86) was used (Table 1). The hydroxyl values were 73, 68, 70, 79, and 85 mg-KOH/g for PEC polyol-0, -9, -16, -20, and -24, respectively. The average hydroxyl functionalities per PEC polyol molecule calculated from the hydroxyl values and $M_{n,Maldi}$ values were 2.75, 2.50, 2.41, 2.29, and 2.10 for PEC polyol-0, -9, -16, -20, and -24, respectively. A sufficiently high OH functionality (>2) ensured the usefulness of the polyols for the preparation PU,[30−32] although the hydroxyl functionality values slightly decreased under increased CO_2 pressure.

In previous studies, the active sites of the DMC catalyst are proposed to be cationic.[33] Typically, epoxide monomer is first coordinated onto the Zn sites to replace complexing agent, followed by transfer reaction to initiator (i.e., glycerol

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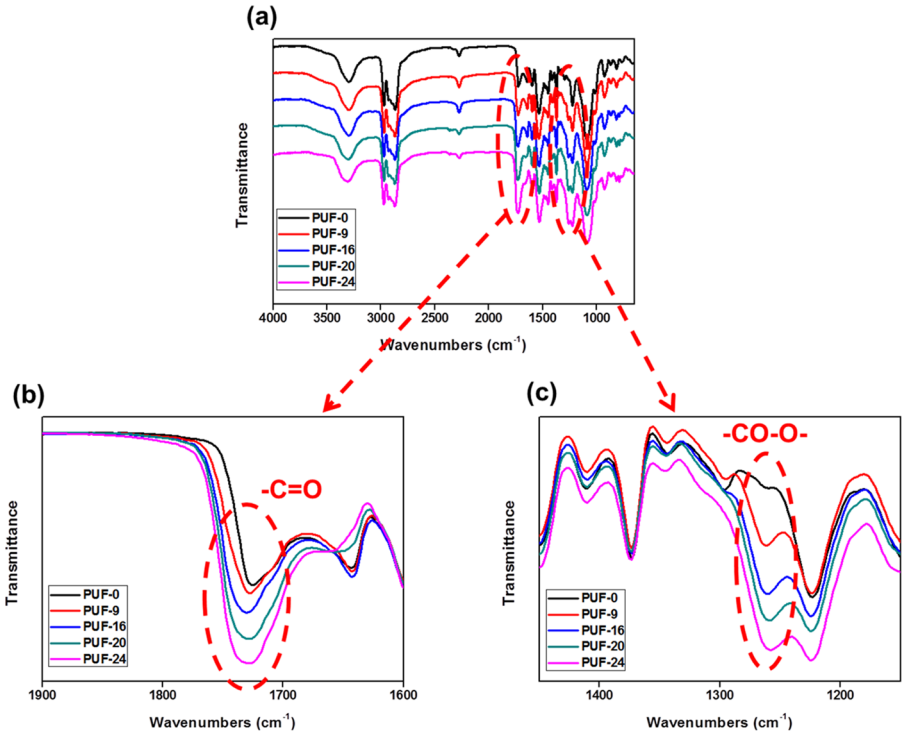

Figure 3. FT-IR spectra of PUFs in the range of 650−4000 cm^{-1} (a): enlarged spectra in the range of 1600−1900 cm^{-1} (b) and 1150−1450 cm^{-1} (c).

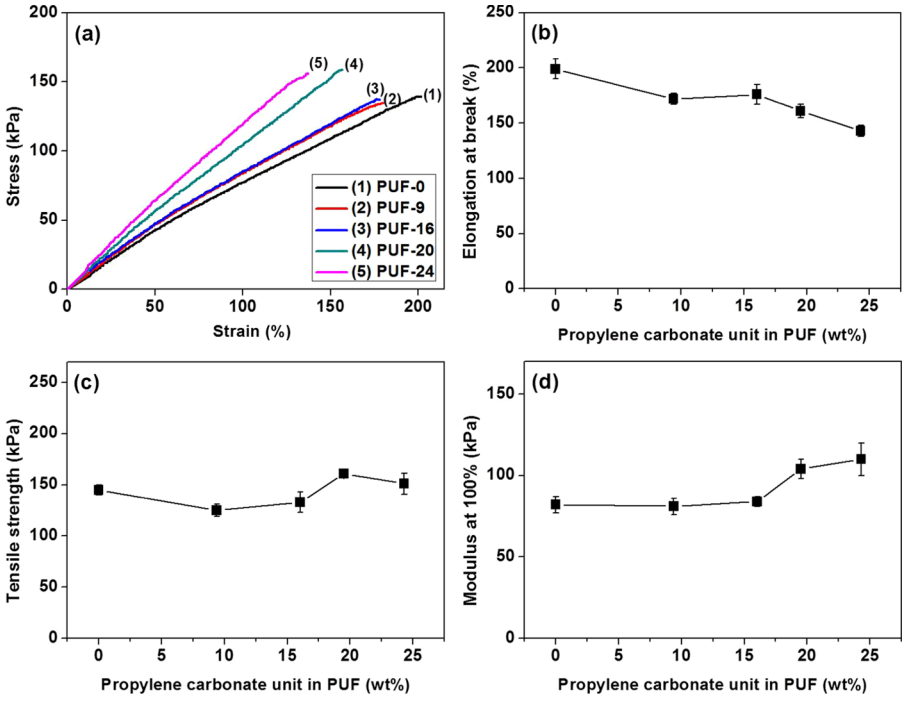

Figure 4. Representative tensile stress−strain curves (a), elongation at break (b), tensile strength (c), and modulus at 100% (d) behaviors of PUFs.

propoxylate in this study) and/or insertion of epoxide monomers for propagation (Figure S5, see the Supporting Information).[34] Zn−O-polymer may then decompose to Zn−OH and HO-polymer to afford polymers with OH groups. Therefore, transfer reaction to initiator should be facilitated to ensure high enough OH functionalities. With increasing CO_2 pressure, both chain-transfer reaction of cationic species to initiator (glycerol propoxylate in this study) and propagation reaction become hindered due to less active carboxylate intermediate, resulting in decreased hydroxyl functionality and molecular weight values of the polymers. Considering the lowered hydroxyl functionality values of the polymers in the presence of CO_2, in this study, initiator with three OH functionality (glycerol propoxylate) was employed to ensure high enough hydroxyl functionality (>2) of the PEC polyols for the preparation of PUFs.

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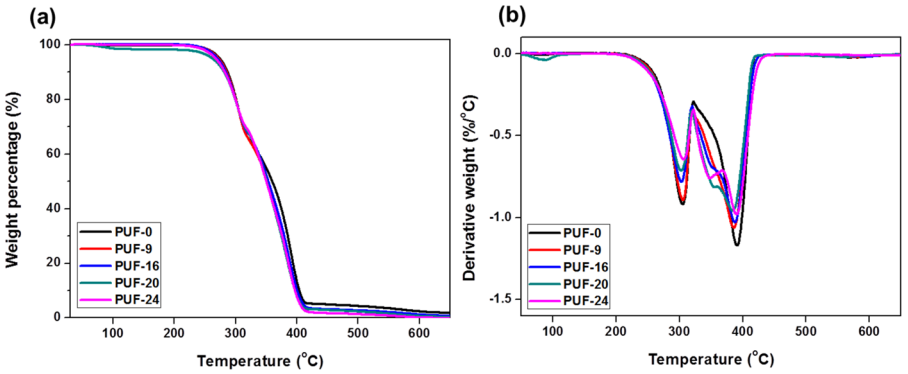

Figure 5. TGA curves (a) and weight-loss derivative curves (b) of PUFs.

PC polyols, such as petroleum-based UH-200 and CO_2-based Converge Polyol 212-20, are waxy solids at room temperature (Figure S6, see the Supporting Information), likely due to rigid carbonate linkages in their chemical structures.[24,35] The solid state of the polyols did not allow their room-temperature use to prepare PUFs following conventional procedures. Proposed solutions to solve the problem include either mixing with liquid PPG, mixing with solvent, or elevating the temperature to melt the waxy polyols. However, the PC polyols exhibited poor miscibility with PPG even at elevated temperature (70 °C, Figure S7, see the Supporting Information), which led to complicated and undesirable reaction kinetics due to mass transfer issues of the components.[36] Mixing the PC polyols with a solvent (e.g., DBE) often caused odorous PUFs with inferior properties due to the presence of solvent. The PC polyols still exhibited high viscosity (for Converge Polyol 212-20, viscosity ∼100 000 cps at 75 °C as reported in its data sheet) and deteriorated reaction kinetics with TDI at elevated temperatures, which did not allow the preparation of PUFs by conventional procedures and facilities.[17] Thus, PEC polyols, which are liquid at room temperature due to inherently flexible ether linkages in their chemical structure, are rationally preferred for the facile and routine preparation of PUF. The PEC polyols prepared in this study were liquid with relatively low viscosity under ambient conditions (582−3082 cps at 25 °C in Table 1), allowing facile and reproducible preparation of PUFs simply by reacting with TDI at room temperature by using conventional facilities.

Scheme 2 demonstrates the successful preparation of foams with similar appearance and density values. The density values of the foams were controlled to be similar to each other (∼39 kg/m^3, Scheme 2) for a reasonable comparison between the samples. The preparation of the foams was quite reproducible, as evidenced by the relatively low-density standard deviation values for repeatedly prepared foams.

The successful preparation of the PUFs was also confirmed by the presence of characteristic peaks of urethane linkage in the FT-IR spectra (Figure 3a).[37] Characteristic FT-IR peaks of −NH at 3390 cm^{-1}, −C═O at 1720−1700 cm^{-1}, −NH−CO at 1530 cm^{-1}, and C−O at 1080 cm^{-1} were distinct, representing urethane linkages. A characteristic remaining peak of −N═C═O was also observed at ∼2270 cm^{-1} due to the excess use of diisocyanate (NCO index = 1.1).[38] As the content of propylene carbonate units increased (W_c values in Table 1), the characteristic peaks of carbonate linkage increased, as shown in Figure 3b (−C═O at 1720−1700 cm^{-1}) and Figure 3c (−CO−O− at 1260 cm^{-1}).

The mechanical properties of the PUFs are presented in Figure 4 and Table S1. Tensile stress−strain curves of the PUFs (Figure 4a) represented typical flexible PUFs with relatively high elongation at break values (Figure 4b). PUF-0 exhibited elongation at break values of ∼199% and modulus values of ∼82 kPa (Table S1), which essentially represent a flexible PUF with conventional PPG-based polyols. Decreased elongation at break values and increased modulus values of the PUFs were observed with increased content of propylene carbonate units (Figure 4b,d and Table S1). The results stemmed from the relatively rigid nature of the carbonate linkage of PEC polyols,[17] indicating that the PUF firmness from the PEC polyols increased with propylene carbonate content. However, PUFs from the PEC polyols with different contents of propylene carbonate units exhibited similar toughness, as evidenced by similar tensile strength values in Figure 4c and Table S1.

The PUFs exhibited a two-step thermal degradation behavior (Figure 5a), which was indicated by the two degradation rate peaks at 300 and 400 °C in their derivative curves (Figure 5b). The first degradation at approximately 300 °C corresponded to the decomposition of the urethane linkage of the PUFs. The second degradation at approximately 400 °C originated from the degradation of polyols. The results indicated that the effect of carbonate linkage content on the thermal stability of PUF is not prominent. Slightly decreased $T_{50\%}$ (temperature at 50% weight-loss in the TGA curve, Table S2) values were observed with an increased content of propylene carbonate units, which was, however, also not so dominant. Interestingly, PUFs with a higher content of carbonate linkage exhibited a relatively lower amount of ash residue (Table S2). The content of ash residue decreased from 3.95 wt % (for PUF-0) to 1.60 wt % (for PUF-24) as the content of propylene carbonate units increased. The result likely stemmed from the clean burning characteristics of the carbonate linkage, which may inversely generate CO_2 during the thermal degradation procedure as reported earlier.[39]

One of the biggest applications of flexible PUF is automobile parts. Recently, VOCs in automobiles have become a prime issue due to increased concerns about the environment and human health, leading increasing legal regulations. In our previous report, we elucidated the importance of compositional factors of PU for reducing the generation of VOCs, notably AA.[27] HS-GC−FID was successfully established for the facile and quantitative monitoring of the generation of AA at different thermal treatment temperatures and times.

The amount of AA generated from PUF-0 (7.66 ppm in Figure 6) was essentially same as that generated from a PUF

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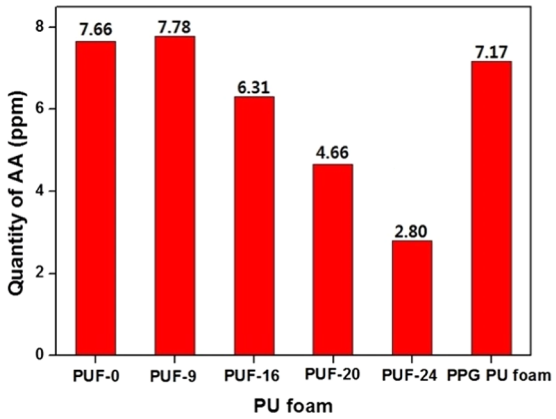

Figure 6. Amount of AA generated from conventional PPG and PUFs with PEC polyols.

with conventional PPG (7.17 ppm in Figure 6) because PUF-0 was composed of polyether-based polyol only (Figure 6). Clearly, the amount of AA generated from the PUFs decreased with increasing content of propylene carbonate units in the polyols (7.78, 6.31, 4.66, and 2.80 ppm for PUF-9, PUF-16, PUF-20, and PUF-24, respectively). The results suggested an improved chemical resistance of the propylene carbonate units in the polyols against the generation of AA during thermo-oxidative degradation. The reduced generation of AA in the PUFs containing carbonate units is also supported by our previous study, where PU with PC polyol exhibited a substantial reduction of AA emissions due to better thermo-oxidative stability of the propylene carbonate units against radical-mediated decomposition.[27] Overall, these studies demonstrated the potential of PUFs with CO_2-based PEC polyols as promising green and low-VOC products that can be easily prepared with conventional facilities under ambient conditions.

CONCLUSIONS

As a sustainable feedstock, a controlled amount of CO_2 was introduced into PEC polyols as propylene carbonate linkages simply by adjusting the CO_2 pressure during the copolymerization with PO in the presence of DMC catalyst. The CO_2-based PEC polyols were liquid and exhibited relatively low viscosity at room temperature, allowing the facile preparation of PUFs with conventional facilities under ambient conditions. The preparation of the foams was quite reproducible, as evidenced by the relatively low standard deviation values of the density for the repeatedly prepared foams. With an increased content of propylene carbonate units, the PUFs exhibited decreased elongation at break values and increased modulus values, indicating firm foams with reasonable toughness. The PUFs with higher contents of carbonate units also exhibited relatively lower amounts of ash residue. Interestingly, a reduced amount of AA was generated from thermo-oxidative degradation of PUF with a high content of propylene carbonate units, suggesting improved chemical resistance of propylene carbonate units of the polyols against the generation of free radicals and AA. These results demonstrated a facile technical pathway to prepare eco-friendly PUFs at ambient conditions from green and renewable CO_2 resources. The PUFs exhibited predictable mechanical properties and low VOC emission characteristics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00808.

Mechanical properties of PUFs; characteristic values of TGA curves of PUFs; photos of pressurized reactor; ^{1}H NMR spectra; MALDI-TOF MS spectra; proposed pathways of DMC-catalyzed polymerization of epoxides; photos of PC polyols (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ilkim@pusan.ac.kr. Tel.: +82-51-510-2466. Fax: +82-51-513-7720 (I.K.).

*E-mail: joonhyun@rist.re.kr. Tel.: +82-54-279-6781. Fax: +82-54-279-6239 (J.H.B.).

*E-mail: sunghong@sejong.ac.kr. Tel.: +82-2-3408-3750. Fax: +82-2-3408-4342 (S.C.H.).

ORCID

Il Kim: 0000-0001-8047-7543

Sung Chul Hong: 0000-0003-0961-7245

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; Dubois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO_2 fixation. *Chem. Rev.* **2013**, *113*, 6621−6658.

(2) Markewitz, P.; Kuckshinrichs, W.; Leitner, W.; Linssen, J.; Zapp, P.; Bongartz, R.; Schreiber, A.; Müller, T. E. Worldwide innovations in the development of carbon capture technologies and the utilization of CO_2. *Energy Environ. Sci.* **2012**, *5*, 7281−7305.

(3) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.* **2007**, *107*, 2365−2387.

(4) Mikkelsen, M.; Jørgensen, M.; Krebs, F. C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.* **2010**, *3*, 43−81.

(5) Cuéllar-Franca, R. M.; Azapagic, A. Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. *J. CO_2 Util.* **2015**, *9*, 82−102.

(6) Darensbourg, D. J.; Holtcamp, M. W. Catalysts for the reactions of epoxides and carbon dioxide. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(7) Langanke, J.; Wolf, A.; Hofmann, J.; Bohm, K.; Subhani, M. A.; Muller, T. E.; Leitner, W.; Gurtler, C. Carbon dioxide (CO_2) as sustainable feedstock for polyurethane production. *Green Chem.* **2014**, *16*, 1865−1870.

(8) Qin, Y.; Wang, X. Carbon dioxide-based copolymers: Environmental benefits of PPC, an industrially viable catalyst. *Biotechnol. J.* **2010**, *5*, 1164−1180.

(9) Kember, M. R.; Buchard, A.; Williams, C. K. Catalysts for CO_2/epoxide copolymerisation. *Chem Commun.* **2011**, *47*, 141−163.

DOI: 10.1021/acsomega.9b00808
ACS Omega 2019, 4, 7944−7952

(10) Qin, Y.; Sheng, X.; Liu, S.; Ren, G.; Wang, X.; Wang, F. Recent advances in carbon dioxide based copolymers. *J. CO_2 Util.* **2015**, *11*, 3−9.
(11) Alagi, P.; Ghorpade, R.; Choi, Y. J.; Patil, U.; Kim, I.; Baik, J. H.; Hong, S. C. Carbon dioxide-based polyols as sustainable feedstock of thermoplastic polyurethane for corrosion-resistant metal coating. *ACS Sustainable Chem. Eng.* **2017**, *5*, 3871−3881.
(12) Darensbourg, D. J.; Yeung, A. D. A concise review of computational studies of the carbon dioxide−epoxide copolymerization reactions. *Polym. Chem.* **2014**, *5*, 3949−3962.
(13) Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. Polyurethane types, synthesis and applications - a review. *RSC Adv.* **2016**, *6*, 114453−114482.
(14) Inoue, S.; Koinuma, H.; Tsuruta, T. Copolymerization of carbon dioxide and epoxide. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287−292.
(15) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. Poly(propylene carbonate). 1. More about poly(propylene carbonate) formed from the copolymerization of propylene oxide and carbon dioxide employing a zinc glutarate catalyst. *Macromolecules* **2002**, *35*, 6494−6504.
(16) Luinstra, G. A. Poly(propylene carbonate), old copolymers of propylene oxide and carbon dioxide with new interests: Catalysis and material properties. *Polym. Rev.* **2008**, *48*, 192−219.
(17) DeBolt, M.; Kiziltas, A.; Mielewski, D.; Waddington, S.; Nagridge, M. J. Flexible polyurethane foams formulated with polyols derived from waste carbon dioxide. *J. Appl. Polym. Sci.* **2016**, *133*, No. 44086.
(18) Von der Assen, N.; Bardow, A. Life cycle assessment of polyols for polyurethane production using CO_2 as feedstock: Insights from an industrial case study. *Green Chem.* **2014**, *16*, 3272−3280.
(19) Wang, J.; Zhang, H.; Miao, Y.; Qiao, L.; Wang, X.; Wang, F. Waterborne polyurethanes from CO_2 based polyols with comprehensive hydrolysis/oxidation resistance. *Green Chem.* **2016**, *18*, 524−530.
(20) Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F. R.; Frey, H. Polymerization of ethylene oxide, propylene oxide, and other alkylene oxides: Synthesis, novel polymer architectures, and bioconjugation. *Chem. Rev.* **2016**, *116*, 2170−2243.
(21) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C. Toward the design of double metal cyanides for the copolymerization of CO_2 and epoxides. *Inorg. Chem.* **2001**, *40*, 6543−6544.
(22) Kim, I.; Yi, M. J.; Lee, K. J.; Park, D.-W.; Kim, B. U.; Ha, C.-S. Aliphatic polycarbonate synthesis by copolymerization of carbon dioxide with epoxides over double metal cyanide catalysts prepared by using ZnX_2 (X = F, Cl, Br, I). *Catal. Today* **2006**, *111*, 292−296.
(23) Chen, S.; Xiao, Z.; Ma, M. Copolymerization of carbon dioxide and epoxides with a novel effective Zn−Ni double-metal cyanide complex. *J. Appl. Polym. Sci.* **2008**, *107*, 3871−3877.
(24) Liu, S.; Miao, Y.; Qiao, L.; Qin, Y.; Wang, X.; Chen, X.; Wang, F. Controllable synthesis of a narrow polydispersity CO_2-based oligo(carbonate-ether) tetraol. *Polym. Chem.* **2015**, *6*, 7580−7585.
(25) Alagi, P.; Ghorpade, R.; Jang, J. H.; Patil, C.; Jirimali, H.; Gite, V.; Hong, S. C. Functional soybean oil-based polyols as sustainable feedstocks for polyurethane coatings. *Ind. Crop. Prod.* **2018**, *113*, 249−258.
(26) Orgilés-Calpena, E.; Arán-Aís, F.; Torró-Palau, A. M.; Montiel-Parreño, E.; Orgilés-Barceló, C. Synthesis of polyurethanes from CO_2-based polyols: A challenge for sustainable adhesives. *Int. J. Adhes. Adhes.* **2016**, *67*, 63−68.
(27) Choi, Y. J.; Alagi, P.; Jang, J. H.; Lee, S. J.; Yoon, H. Y.; Hong, S. C. Compositional elements of thermoplastic polyurethanes for reducing the generation of acetaldehyde during thermo-oxidative degradation. *Polym. Test.* **2018**, *68*, 279−286.
(28) Lim, J.; Yun, S. H.; Kim, M.-R.; Kim, I. Synthesis of polycarbonate polyols by double-metal cyanide catalyzed copolymerization of epoxide with carbon dioxide. *J. Nanosci. Nanotechnol.* **2017**, *17*, 7507−7514.
(29) Zhang, X.-H.; Wei, R.-J.; Sun, X.-K.; Zhang, J.-F.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures. *Polymer* **2011**, *52*, 5494−5502.
(30) Alagi, P.; Ghorpade, R.; Jang, J. H.; Patil, C.; Jirimali, H.; Gite, V.; Hong, S. C. Controlled hydroxyl functionality of soybean oil-based polyols for polyurethane coatings with improved anticorrosion properties. *Macromol. Res.* **2018**, *26*, 696−703.
(31) Alagi, P.; Choi, Y. J.; Seog, J.; Hong, S. C. Efficient and quantitative chemical transformation of vegetable oils to polyols through a thiol-ene reaction for thermoplastic polyurethanes. *Ind. Crop. Prod.* **2016**, *87*, 78−88.
(32) Alagi, P.; Choi, Y. J.; Hong, S. C. Preparation of vegetable oil-based polyols with controlled hydroxyl functionalities for thermoplastic polyurethane. *Eur. Polym. J.* **2016**, *78*, 46−60.
(33) Kim, I.; Ahn, J.-T.; Ha, C. S.; Yang, C. S.; Park, I. Polymerization of propylene oxide by using double metal cyanide catalysts and the application to polyurethane elastomer. *Polymer* **2003**, *44*, 3417−3428.
(34) Tran, C. H.; Pham, L. T. T.; Lee, Y.; Jang, H. B.; Kim, S.; Kim, I. Mechanistic insights on Zn(II)−Co(III) double metal cyanide-catalyzed ring-opening polymerization of epoxides. *J. Catal.* **2019**, *372*, 86−102.
(35) Park, J. E.; Kim, W. K.; Hwang, D. Y.; Choi, G. H.; Suh, D. H. Thermally stable bio-based aliphatic polycarbonates with quadracyclic diol from renewable sources. *Macromol. Res.* **2018**, *26*, 246−253.
(36) Wenning, C.; Noe, J.; Barbe, S.; Leimenstoll, M. C. Evidence of liquid-liquid demixing during bi-soft segment polyurethane prepolymerization. *Macromol. Res.* **2018**, *26*, 395−398.
(37) Li, Y.; Ren, H.; Ragauskas, A. J. Rigid polyurethane foam reinforced with cellulose whiskers: Synthesis and characterization. *Nano-Micro Lett.* **2010**, *2*, 89−94.
(38) Pillai, P. K. S.; Li, S.; Bouzidi, L.; Narine, S. S. Solvent-free synthesis of polyols from 1-butene metathesized palm oil for use in polyurethane foams. *J. Appl. Polym. Sci.* **2016**, *133*, No. 43509.
(39) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, J. H.; Jeon, J. Y.; Kim, S. J.; Lee, B. Y. Preparation of flame-retarding poly(propylene carbonate). *Green Chem.* **2011**, *13*, 3469−3475.

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ACS Omega 2019, 4, 7944−7952