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Novel Polyurethane-Catalyzed Cyclic Carbonate Synthesis Using CO_2 and Epoxide

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ABSTRACT. The conversion of industrially produced greenhouse gases, like CO_2, into value-added chemicals is economically beneficial to industry and vital for environmental conservation. However, the conditions for these conversions must themselves be sustainable. In this work, polyurethane (PU) was used to catalyze the formation of five-membered cyclic carbonates (5CCs) via cycloaddition of epoxides and CO_2. Using optimized conditions, the representative epoxide, phenyl glycidyl ether, afforded the corresponding 5CC (PGE-5CC) in quantitative yield with remarkable selectivity (>99%). The PU catalyst does not degrade during the reaction and is separable by simple filtration. In addition, PU could catalyze the 5CC synthesis at least ten times without loss of the catalytic activity and is applicable to a wide range of substituted epoxides. This study pioneers the utilization of polyurethane as an easily recycled catalyst in halogen- and metal-free reactions for the repurposing of CO_2 waste.

KEYWORDS: Cycloaddition, Organocatalyst, Metal-free synthesis, Halogen-free synthesis, Sustainable chemistry, Eco-friendly chemistry

INTRODUCTION

CO_2 is an inexpensive, nontoxic, nonflammable, and abundant carbon resource, rendering its use in organic synthesis via one-carbon (C1) chemistry both economically and conservationally significant. One widely reported transformation using CO_2 involves the cycloaddition of epoxides to form five-membered cyclic carbonates (5CCs).[1-4] These 5CCs can be used for a variety of applications including aprotic solvents, fuel additives, and lithium-ion battery electrolytes,[5] isocyanate-free synthesis of polyurethanes.[6]

Organocatalysts[7-9] have garnered significant interest for the synthesis of 5CCs, as they are generally cost-effective, sustainable, and less toxic than metal-based[10-11]catalysts. Among them, halogen-free conditions in the synthetic process for 5CCs is essential if these reactions seek to prevent environmental pollution and further the goals of sustainable chemistry.[12] Therefore, the development of highly selective catalytic systems using inexpensive, metal- and halogen-free compounds is critical for the effective manufacturing of 5CCs.

Herein, we report the use of polyurethane (PU) as an organocatalyst for the conversion of epoxides to 5CCs. Thus far, the treatment of PU waste has been a topic of concern. As one of the treatments, hydrolytic decomposition of PU has been studied,[13] and then this work potentially provides for new functionalization and application of PU waste.

RESULTS AND DISCUSSTION

Catalytic activity for the synthesis of 5CCs was evaluated using PU[13] (Scheme 1). PU is insoluble in common organic solvents, and should therefore be easily separable by filtration from the reaction mixture when used as a catalyst.

The original epoxide used for this study was phenyl glycidyl ether (PGE). PGE was heated at 150 °C for 42 h under 9.0 MPa pressure of CO_2, in which a molar ratio of [urethane group of

PU]$_0$/[PGE]$_0$ was 0.2, equal to 20 mol% catalyst. After 42 h, $CDCl_3$ was added to the reaction mixture, which was then filtered to remove the insoluble residual solid.

The compounds in solution were characterized by ^{1}H-NMR, with signals attributable to both PGE and newly appeared PGE-derived 5CC[7] (PGE-5CC), (Figure S1, in Supporting Information (SI)). The conversion of PGE and the selectivity of the reaction for the production of PGE-5CC were 49% and >99%, respectively. The isolated yield of PGE-5CC by column chromatography was 47%, which was in excellent agreement with the estimated value for PGE conversion. These results are in stark contrast with the reaction performed in the absence of PU, in which no reaction occurred, indicating that PU is essential for the cycloaddition of PGE with CO_2.

The insoluble residual solid from the reaction was analyzed and the results were compared with those of pure PU. The FT-IR spectra of both PU and the solid showed absorption bands at 3321, 2961, 2890, 1701, 1528, and 1227 cm^{-1} (Figure S2, SI). The ^{1}H-NMR spectra of both PU and the solid displayed the same chemical shifts and integral ratios (Figure S3, SI). In addition, the gel permeation chromatography profiles of PU and the solid were almost identical (Figure S4, SI). The number- and weight-average molecular weights and dispersity values were also found to be similar (Table S1, SI). These results demonstrate that the insoluble solid material is PU and confirm that PU is not degraded during the reaction and can be easily separated from the reaction by filtration.

To probe the effects of the reaction conditions on the yield of PGE-5CC, temperature, pressure of CO_2, and reaction time were varied, with the molar ratio of [urethane group of PU]$_0$/[PGE]$_0$ held constant at 1.0 (Table S2, SI). The yields of PGE-5CC gradually increased with increasing reaction time, reaching a quantitative value at 48 h (Entry 1−5). As for the pressure-dependence at reaction time of 6 h (Entry 2, 6−8), the yields increased with increasing pressure of CO_2 but

began to plateau beyond 4.9 MPa. Importantly, all reactions displayed excellent selectivity for PGE-5CC (>99%). Regarding the temperature-dependence of the reaction, increasing the temperature in the range of 120−180 °C (Entry 3, 9, and 10) resulted in drastic changes in the yields. However, the selectivity decreased slightly at 180 °C, and new unassignable signals were detected in the ^{1}H-NMR spectrum of the reaction mixture.

Finally, we varied the quantity of PU to determine its catalytic activity (Table 1). Increasing the ratio from 0.1 to 0.4, the yield increased. Especially, for the elongated reaction time to 72 h, the yields were increased to 73% and 98% even with the ratio of 0.2 and 0.4, respectively. The yield was obviously higher than the ratio using the urethane moiety, indicating that PU acts as a catalyst in the cycloaddition of epoxide to CO_2. In the large-scale synthesis using 10 g PGE, a 51 % yield was also obtained under same conditions and ratio as Entry 5 (47% yield) in Table 1.

To confirm the reusability of PU, the catalytic activity of the obtained insoluble residual solid (used-PU) was reexamined in the PGE cycloaddition. The used-PU was reapplied to the optimized reaction (150 °C, 6 h, 9.0 MPa pressure of CO_2) using the molar ratio of 1.0. The reaction cycle (reaction, filtration, drying) was repeated ten times in succession. The yields in every reaction were consistently constant values ranging between 45−50% over all ten reaction cycles (Figure S5, SI), indicating that the PU catalyst can be reused without loss of activity. This is in excellent agreement with the lack of PU degradation after the initial reaction (Figure S2−S4, SI). In the repeated reaction cycles mentioned above, GPC profiles, and ^{1}H-NMR and FT-IR spectra were also maintained (Figure S6−S9, SI).

Having successfully produced PGE-5CC, we next evaluated the scope of the PU-catalyzed cycloaddition reaction using a range of epoxides to obtain the corresponding 5CCs (Scheme 2). These reactions successfully gave the corresponding 5CCs in 31%−almost quantitative yields

with good selectivity except for **5CC-7** (87% selectivity). These results revealed that the PU-catalyzed reaction can be applied to a spectrum of epoxides. Using optically active epoxides, optically active **5CC-8** and **5CC-9** were obtained, suggesting an S_N2 type reaction mechanism.[7]

We propose the following mechanism for the PU-catalyzed formation of 5CC (Scheme 3). The urethane group activates the epoxide via hydrogen bonding with the epoxide oxygen (path A). Nucleophilic attack by the urethane carbonyl oxygen atom[14–15] on the epoxide ring (path B) results in epoxide ring-opening and subsequent formation of an alkoxide ion. This alkoxide ion then attacks CO_2, resulting in the formation of the carbonate ion (path C), followed by ring-closure to release the PU and generate the 5CC product (path D).

CONCLUSION

We found that the stable, abundant, and easy-to-handle polymer, PU, catalyzes the reaction of epoxides with CO_2 to form 5CCs. Polyurethane structure-activity relationships, molecular weight-dependency, and evaluation of the reaction intermediates are currently underway to further understand and expand upon the findings of this study.

ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge.

Reagents; Synthesis and characterization; ^{1}H-NMR and FT-IR spectra, GPC profiles and SEM image of PU; Table of effect of the reaction conditions; Procedure and data in recycling experiment; Characteristic data of 5CCs (PDF)

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Author Contributions

The manuscript was written through contribution of all authors. All authors gave approval to the final version of the manuscript.

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ABBREVIATIONS

5CC, five-membered cyclic carbonate; C1, one-carbon; PGE, phenyl glycidyl ether; PGE-5CC phenyl glycidyl ether-derived five-membered cyclic carbonate; PU, polyurethane.

REFERENCES

[1] Yu, B.; Zou, B.; Hu, C.-W. Recent applications of polyoxometalates in CO_2 capture and transformation. *J. CO_2 Util*. **2018**, *26*, 314−322, DOI: https://doi.org/10.1016/j.jcou.2018.05.021.

[2] Alper, E.; Orhan, O. Y. CO_2 utilization: Developments in conversion processes. *Petroleum* **2017**, *3* (1), 109−126, DOI: https://doi.org/10.1016/j.petlm.2016.11.003.

[3] Büttner, H.; Longwitz,L.; Steinbauer, J.; Wulf, C.; Werner, T. Recent Developments in the Synthesis of Cyclic Carbonates from Epoxides and CO_2. In *Chemical Transformations of Carbon Dioxide*; Wu, X.-F.; Beller, M. Eds.; Springer Nature: Switzerland, **2017**; pp 89−144, DOI: 10.1007/s41061-017-0136-5.

[4] Cokoja, M.; Wilhelm, M. E.; Anthofer, M. H.; Herrmann, W. A.; Kühn, F. E. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts. *ChemSusChem*, **2015**, *8* (15), 2436−2454, DOI: 10.1002/cssc.201500161.

[5] Zhao, C.; Luo, X.; Chen, C.; Wu, H. Sandwich electrode designed for high performance lithium-ion battery. *Nanoscale* **2016**, *8*, 9511−9516, DOI: 10.1039/C5NR09049K.

[6] Yadav, N.; Seidi, F.; Crespy, D.; D'Elia, V. Polymers Based on Cyclic Carbonates as *Trait d'Union* Between Polymer Chemistry and Sustainable CO_2 Utilization. *ChemSusChem* **2019**, *12* (4), 724−754, DOI: 10.1002/cssc.201802770.

[7] Kihara, N.; Hara, N.; Endo, T. Catalytic activity of various salts in the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide under atmospheric pressure. *J. Org. Chem.* **1993**, *58* (23), 6198−6202, DOI: 10.1021/jo00075a011.

[8] Wang, L.; Zhang, G.; Kodama, K.; Hirose, T. An efficient metal- and solvent-free organocatalytic system for chemical fixation of CO_2 into cyclic carbonates under mild conditions. *Green Chem.* **2016**, *18*, 1229−1233, DOI: 10.1039/C5GC02697K.

[9] Peng, J.; Wang, S.; Yang H.-J.; Ban, B.; Wei, Z.; Wang, L.; Lei, B. Chemical fixation of CO_2 to cyclic carbonate catalyzed by new environmental- friendly bifunctional bis-β-cyclodextrin derivatives. *Catal. Today* **2019**, *330*, 76−84, DOI: 10.1016/j.cattod.2018.06.020.

[10] Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. Mg−Al Mixed Oxides as Highly Active Acid−Base Catalysts for Cycloaddition of Carbon Dioxide to Epoxides. *J. Am. Chem. Soc.* **1999**, *121* (18), 4526−4527, DOI: 10.1021/ja9902165.

[11] Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C. Nb(V) compounds as epoxides carboxylation catalysts: the role of the solvent. *J. Mol. Catal. A: Chem.* **2003**, *204−205*, 245−252, DOI: 10.1016/S1381-1169(03)00305-4.

[12] Zou, B.; Hu, C. Halogen-free processes for organic carbonate synthesis from CO_2. *Curr. Opin. Green Sustainable Chem.* **2017**, *3*, 11−16, DOI: 10.1016/j.cogsc.2016.10.007.

[13] Motokucho, S.; Yamaguchi, A.; Nakayama, Y.; Morikawa, H.; Nakatani, H. Hydrolysis of aromatic polyurethane in water under high pressure of CO_2. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (12), 2004−2010, DOI: 10.1002/pola.28576.

[14] Carpino, L. A.; Parameswaran, K. N., Kirkley, R. K.; Spiewak, J. W.; Schmitz, E. New methods of introducing the carbo-tert-butoxy amino-protecting group. tert-Alkyl chloroformates substituted with electron-withdrawing substituents. *J. Org. Chem.* **1970**, *35* (10), 3291−3295, DOI: 10.1021/jo00835a025.

[15] Ohnishi, T.; Sugano, H.; Muneji, M. The Synthesis and Reaction of Monohalogeno-*t*-butyloxycarbonylamino Acids. *Bull. Chem. Soc. Jpn.* **1972**, *45* (8), 2603−2607, DOI: 10.1246/bcsj.45.2603.

SCHEME CAPTIONS

Scheme 1. PU-catalyzed cycloaddition of epoxides to CO_2.

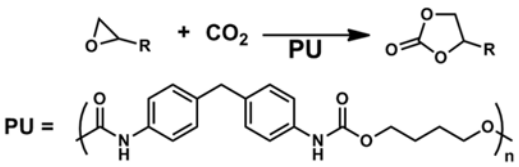
Scheme 2. Synthesis of 5CCs from CO_2 with various epoxides.

Scheme 3. Proposed reaction mechanism for PU-catalyzed cycloaddition of epoxide and CO_2.

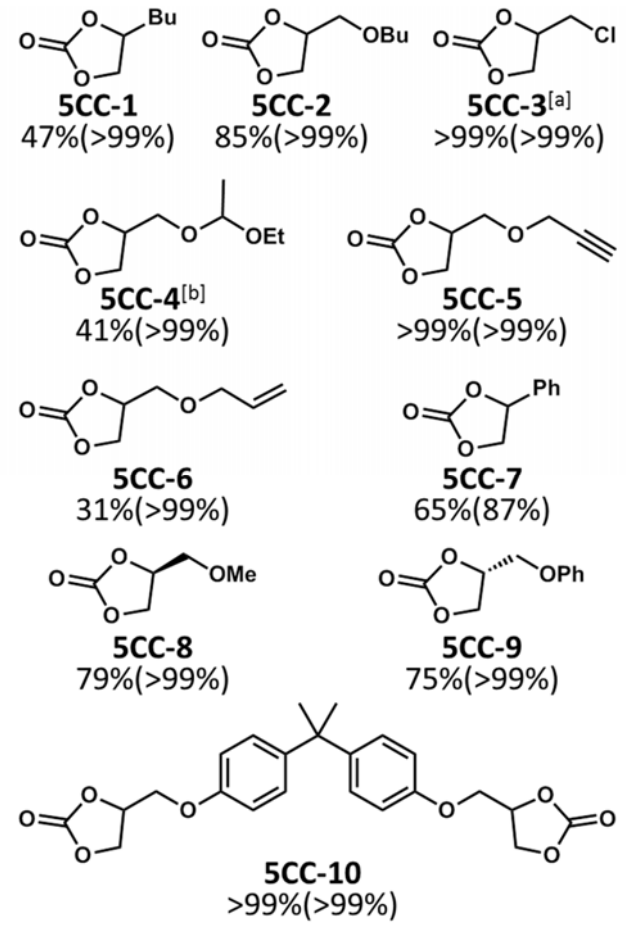
Table 1. Effects of the reaction conditions on the synthesis of PGE-5CC.

SCHEMES

Scheme 1. PU-catalyzed cycloaddition of epoxides to CO_2.

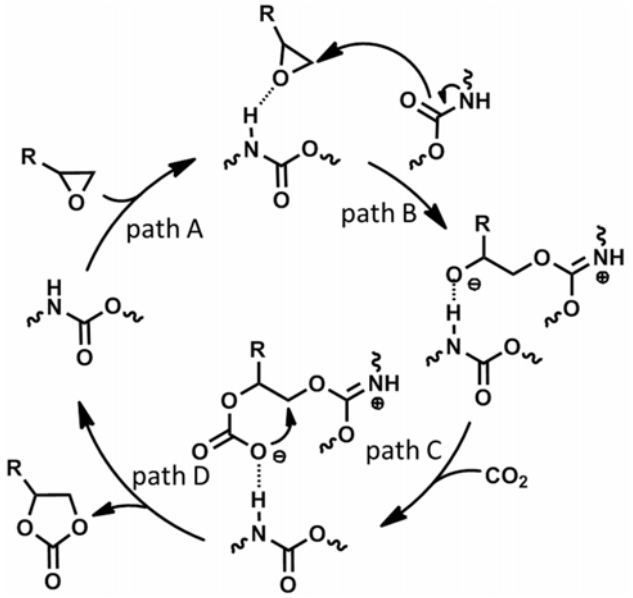


Scheme 2. Synthesis of 5CCs from CO_2 with various epoxides.



Reaction conditions: 150 °C, 9.0 MPa of CO_2, for 16 h, epoxide (5.0 mmol), [urethane group of PU]$_0$/[epoxide]$_0$ = 1.0. Selectivity for 5CC, given in parenthesis, was determined from the 1H-NMR spectrum of an aliquot of the reaction mixture. Reaction times were [a] 4 h, and [b] 72 h.

Scheme 3. Proposed reaction mechanism for PU-catalyzed cycloaddition of epoxide and CO_2.



TABLE

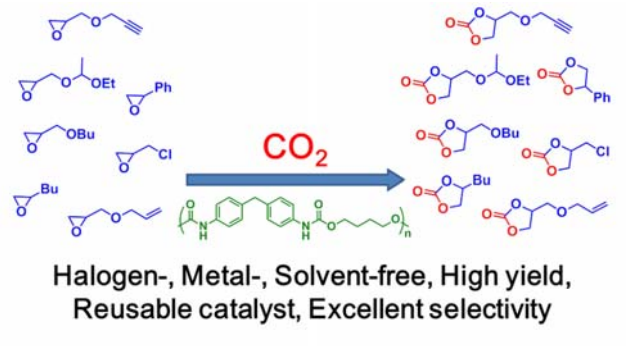
Table 1. Effects of the reaction conditions on the synthesis[a] of PGE-5CC.

Entry	Time/h	[urethane group of PU]$_0$/[PGE]$_0$	Isolated yield of PGE-5CC (selectivity)/%[b]
1	16	0.1	14 (>99)
2	42	0.1	39 (>99)
3	72	0.1	52 (>99)
4	16	0.2	26 (>99)
5	42	0.2	47 (>99)
6	72	0.2	73 (>99)
7	16	0.4	50 (>99)
8	42	0.4	96 (>99)
9	72	0.4	98 (>99)

[a]Condition: 150 °C and 9.0 MPa CO_2.

[b]Selectivity for PGE-5CC, given in parenthesis, was determined from the ^{1}H-NMR spectrum of an aliquot of the reaction mixture.

TOC and SYNOPSIS



SYNOPSIS.
A sustainable approach for recycling CO_2 into value-added reagents in high yield was achieved with a reusable polyurethane catalyst.

Supporting Information

Novel Polyurethane-Catalyzed Cyclic Carbonate Synthesis using CO_2 and Epoxide

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Totals – 13 pages, 9 figures and 3 tables

Table of Contents

1. Materials and methods

All reagents were used without further purification unless otherwise stated. *N*,*N*-Dimethylacetamide (DMAc), phenyl glycidyl ether (PGE), 2-phenyloxirane and 2-(chloromethyl)oxirane were obtained from WAKO Chemicals Co., Ltd. (Osaka, Japan). 2-butyloxirane, 2-(butoxymethyl)oxirane, 2-((1-ethoxyethoxy)methyl)oxirane, 2-((prop-2-yn-1-yloxy)methyl)oxirane, 2-((allyloxy)methyl)oxirane, (*R*)-2-(methoxymethyl)oxirane, (*S*)-2-(phenoxymethyl)oxirane and 2,2'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(oxirane) were obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). 4,4'-Diphenylmethane diisocyanate (MDI) was obtained from Nippon Polyurethane Industry Co. Ltd. (Yamaguchi, Japan). Chloroform-*d* ($CDCl_3$) and dimethyl sulfoxide-d_6 (DMSO-d_6) were obtained from Sigma-Aldrich Japan Co., Ltd. (Tokyo, Japan). All other reagents and solvents were obtained from commercial sources. *N*,*N*-Dimethylformamide (DMF) and 1,4-butanediol (BD) were obtained from WAKO Chemicals Co., Ltd. and were used after following distillation under reduced pressure.

IR spectra were recorded using a Bio-Rad Laboratories FTS 3000MXN (Osaka, Japan), and the values are reported in cm^{-1}. ^1H and ^{13}C nuclear magnetic resonance (^1H- and ^{13}C-NMR) spectra were obtained using a JNM-GX400 (JEOL, Ltd., Japan) at 400 MHz and 100 MHz, respectively. Values are reported in ppm. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity index ($Đ$, M_w/M_n) were estimated by gel permeation chromatography (GPC) on a polystyrene gel column (KF-803L; Shodex Co. Ltd., Japan) using a JASCO (JASCO Corp., Japan) HPLC system (pump; PU-2060, reflective index detector; RI-2031, column oven; CO-4060) with a DMF (containing 10 mmol/L LiBr) eluent at a flow rate of 1.0 mL/min. The system was calibrated using polystyrene standards. The SEM observations were carried out with a JEOL JSM-7500FAM at 2 kV. The PU was sputter coated with gold. Optical rotations were measured in a 50 mm length cell on a JASCO Model P-2200 digital polarimeter at 20 and 21 °C, and an average value from ten measurements was calculated.

2. Synthesis and characterization

Synthesis of poly(methylene bis-(1,4-phenylene)hexamethylene dicarbamate (PU). BD (3.26 g, 36.2 mmol) was added to a solution of MDI (8.88 g, 35.5 mmol) in DMF (70 mL) at 60 °C. The reaction was then heated at 80 °C for 1.5 h. The reaction was monitored for consumption of the isocyanate group by titration with dibutylamine. Upon completion, the reaction mixture was poured into methanol, resulting in the precipitation of a white solid. The resulting precipitate was filtrated, washed with methanol using a Soxhlet extractor, and dried *in vacuo* to give PU as a white solid (8.75 g, 72.1%). The obtained PU was found to be insoluble in the majority of common laboratory solvents, including methanol, ethanol, toluene, chloroform, hexane, ethyl acetate, and water. Highly polar amide or sulfoxide solvents, such as DMF, DMAc, and DMSO, were capable of solubilizing PU. The SEM image of PU was shown in Figure S9.

IR (KBr): 3321 (ν(N-H)$_{H\text{-}bond}$), 2961($\nu_{as}(CH_2)$), 2890($\nu_s(CH_2)$), 1701 (ν(C=O)$_{H\text{-}bond}$), 1528 (ν(C-N), (N-H)), 1227 (ν(C-O)) cm^{-1}.

^1H-NMR (400 MHz, DMSO-d_6): δ 9.53 (broad, 2H), 7.37−7.35 (broad, 4H), 7.10−7.08 (broad, 4H), 4.10 (broad, 4H), 3.78 (broad, 2H), 1.70 (broad, 4H).

$M_n = 4.1 \times 10^4$, $M_w = 6.3 \times 10^4$, $Đ = 1.5$

5% weight loss temperature (T_{d5}) = 293 °C.

Estimation of molar ratio of urethane group ([urethane group of PU]$_0$) to PGE

The mole of urethane group into PU was estimated by the following equation (1).

$$[\mathbf{urethane\ group}]_0 = \frac{[\mathbf{weight\ of\ PU\ (g)}]}{[\mathbf{molecular\ weight\ of\ repeating\ unit\ of\ PU}[340.37]]} \times 2 \quad \text{-(1)}$$

From amount by mole of the urethane group and PGE, the molar ratio of [urethane group]$_0$/[PGE]$_0$ was defined.

General procedure. A mixture of phenyl glycidyl ether (PGE) (0.75 g, 5.0 mmol) and PU (0.17 g, 1.0 mmol of urethane group) (molar ratio of [urethane group]$_0$ / [PGE]$_0$ = 0.2) was placed in a 200 mL autoclave and treated with liquid CO_2 (39 g, 890 mmol). To weight the introduced CO_2, the autoclave before and after introducing CO_2 weighed with electronic balance BPS6K01 (Asone, Japan; resolution of 0.1 g and capability of 6.000 kg). The reaction mixture contained a suspended white solid of PU. Within the autoclave, the mixture was heated with stirring at 150 °C under 9.0 MPa pressure of CO_2. After 42 h, the autoclave was cooled and depressurized. $CDCl_3$ (*ca*. 2 mL) was added to the reaction mixture and the resulting suspension was filtered to separate the insoluble residual solids from solution. An aliquot of the filtrate was analyzed by ^{1}H-NMR to allow for the estimation of PGE conversion and selectivity for PGE-5CC. The filtrate was then concentrated under reduced pressure using a rotary evaporator, and the resulting residue was purified by short column chromatography on silica gel using mixed organic solvent (hexane/ethyl acetate = 2/1, v/v) as the eluent to obtain PGE-5CC as a white solid (0.46 g, 47% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.8 Hz, 2H), 7.02 (m, 1H), 6.91 (d, J = 7.8 Hz, 2H), 5.05−5.00 (m, 1H), 4.61(t, J = 8.4 Hz, 1H), 4.53 (dd, J = 5.9, 8.4 Hz, 1H), 4.24 (dd, J = 4.3, 10.6 Hz, 1H), 4.14 (dd, J = 3.6, 10.6 Hz, 1H).

This reaction, purification, and analysis were individually carried out to evaluate the effects of changes in reaction time (3−72 h), temperature (120−180 °C), and pressure (2.0−9.0 MPa pressure of CO_2) on PGE conversion, and its selectivity for PGE-5CC.

Larger-scale synthesis. A mixture of PGE (10.0 g, 66.60 mmol) and PU (2.27 g, 13.33 mmol of urethane group) in a 200 mL autoclave was heated at 150 °C for 42 h under 9.0 MPa of CO_2. After cooled to room temperature, the reaction mixture was analyzed as the above procedure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 2/1, v/v, as an eluent) to afford PGE-5CC (6.59 g, 51% yield).

Recycled experiments. A mixture of PGE (0.75 g, 5.0 mmol) and PU (0.85 g, 5.0 mmol of urethane group) (molar ratio of [urethane group]$_0$ / [PGE]$_0$ = 1.0) was placed in a 200 mL autoclave and fulfilled with liquid CO_2 (39 g, 890 mmol). The reaction mixture contained a suspended white solid of PU. Within the autoclave, the mixture was heated with stirring at 150 °C under 9.0 MPa pressure of CO_2. After 6 h, the autoclave was cooled and depressurized. $CDCl_3$ (*ca*. 2 mL) was added to the reaction mixture and the resulting suspension was filtered to separate the insoluble residual solids from the solution. An aliquot of the filtrate was analyzed by ^{1}H-NMR to allow for the estimation of PGE conversion and selectivity for PGE-5CC. The filtrate was then concentrated under reduced pressure using a rotary evaporator, and the resulting residue was purified by short column chromatography on silica gel using mixed organic solvent (hexane/ethyl acetate = 2/1, v/v) as the eluent to obtain PGE-5CC as a white solid. The obtained insoluble solid in this reaction was washed with 30mL of $CHCl_3$, and dried under vacuum under reduced pressure overnight and weighted. The dried insoluble solid was again placed in autoclave with PGE and the mixture was heated with stirring at 150 °C under 9.0 MPa pressure of CO_2 for 6 h. This procedure was repeated ten times.

The SEM images of the initial PU and used-PU after the repeated reaction ten times were shown in Figure S9.

Reaction with a range of substituted epoxide with CO_2.

General procedure for the synthesis of 5CC-1 as the typical example. A mixture of 2-butyloxirane (0.50 g, 5.0 mmol) and PU (0.85 g, 5.0 mmol of urethane group) (molar ratio of [urethane group]$_0$ / [PGE]$_0$ = 1.0) was placed in a 200 mL autoclave and treated with liquid CO_2 (39 g, 890 mmol). The reaction mixture contained a suspended white solid of PU. Within the autoclave, the mixture was heated with stirring at 150 °C under 9.0 MPa pressure of CO_2. After 16 h, the autoclave was cooled and depressurized. $CDCl_3$ (*ca*. 2 mL) was added to the reaction mixture and the resulting suspension was filtered to separate the insoluble residual solids from solution. An aliquot of the filtrate was analyzed by ^{1}H-NMR to allow for the estimation of epoxide conversion and selectivity for **5CC-1**. The filtrate was then concentrated under reduced pressure

using a rotary evaporator, and the resulting residue was purified by short column chromatography on silica gel using mixed organic solvent (hexane/ethyl acetate = 4/1, v/v) as the eluent to obtain **5CC-1** as a colorless oil (0.34 g, 47% yield).

3. Estimation of conversion and selectivity by ^{1}H-NMR (See Figure S1)

The conversion of PGE and selectivity for PGE-5CC were estimated using the following equations (2), (3):

$$\text{Conversion of PGE (\%)} = \frac{[(X + Y) / 3] - f}{(X+Y) / 3} \times 100 \quad \text{–(2)}$$

$$\text{Selectivity of the reaction for the production of 5CC (\%)} = \frac{F / [(X + Y) / 3]}{[[(X + Y) / 3] - f] / [(X + Y) / 3]} \times 100$$

$$= \frac{F}{[(X + Y) / 3] - f} \times 100 \quad \text{–(3)}$$

where f = integral ratio of PGE methine protons (from Figure S1)

F = integral ratio of PGE-5CC methine protons (from Figure S1)

X = integral ratio of PGE-5CC aromatic protons (*A,C* from Figure S1) at positions 2,4,6

Y = integral ratio of PGE aromatic protons (*a,c* from Figure S1) at positions 2,4,6

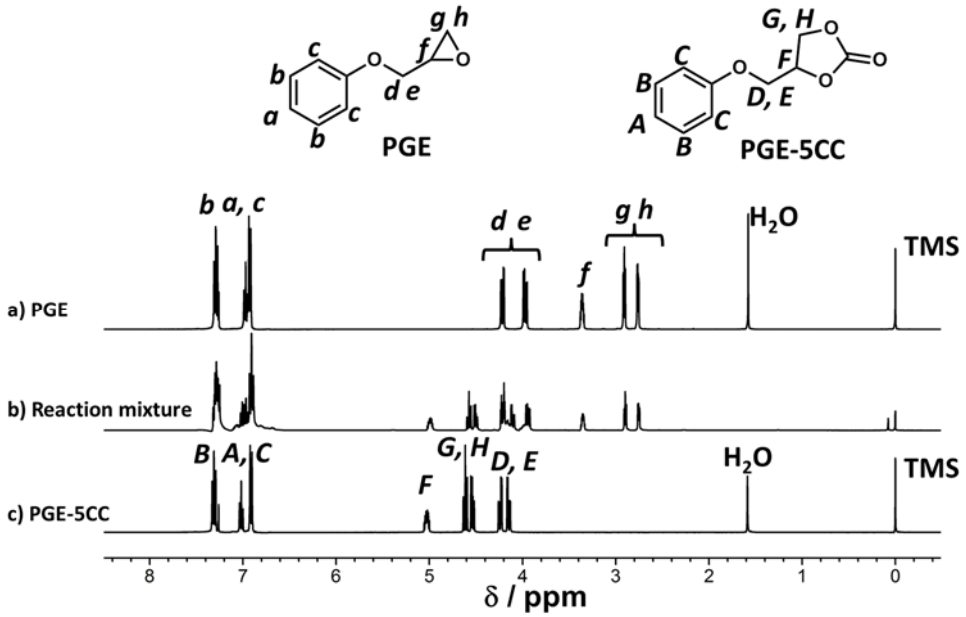


Figure S1. ^{1}H-NMR ($CDCl_3$) spectra of a) PGE b) reaction mixture and c) PGE-5CC. Reaction conditions: 150 °C, 42 h, and 9.0 MPa pressure of CO_2 in the presence of PU ($[\text{urethane group}]_0$ / $[\text{PGE}]_0$ = 0.2).

The sample in Figure S1(b) involved both PGE and the PGE-5CC. From the integrated ratio, the molar ratio of PGE to PGE-5CC could be calculated.

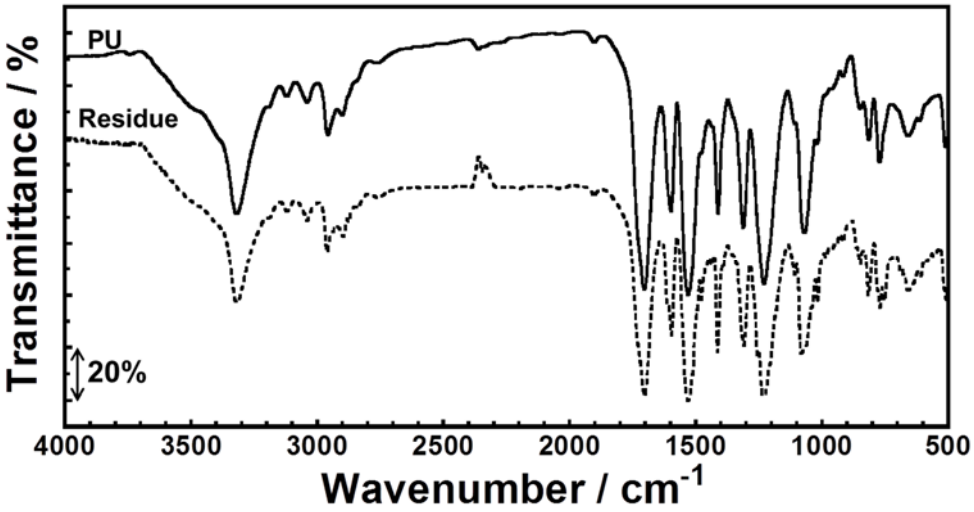


Figure S2. FT-IR spectra of PU (solid line) and the insoluble residual solid obtained by filtration (dotted line).

The peaks of spectra of both samples were observed at same wavenumbers.

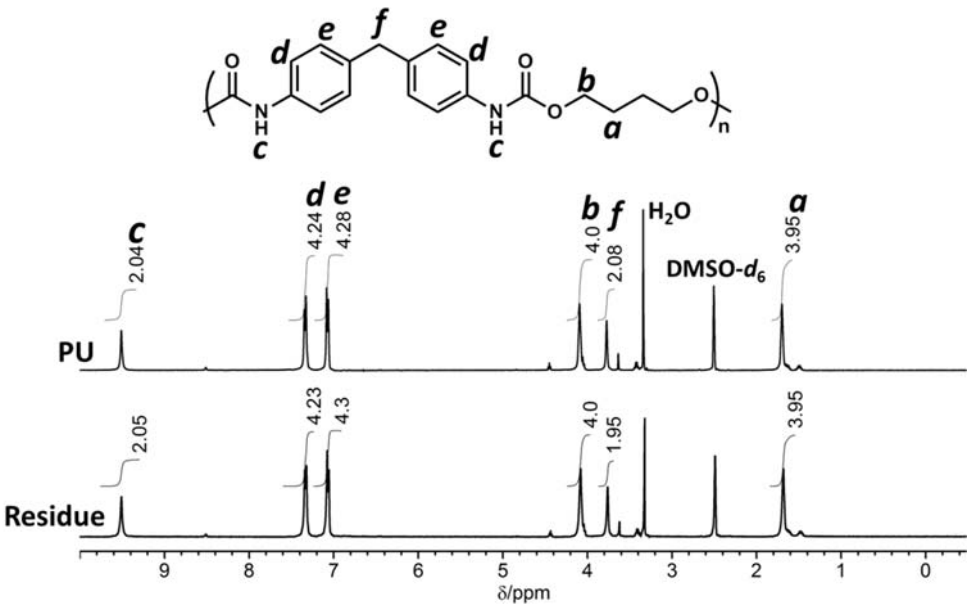


Figure S3. ^{1}H-NMR (DMSO-d_6) spectra of PU (top) and insoluble residual solid obtained by filtration (bottom).

The signals of spectra of both samples were observed at same chemical shifts with almost same integrated ratios.

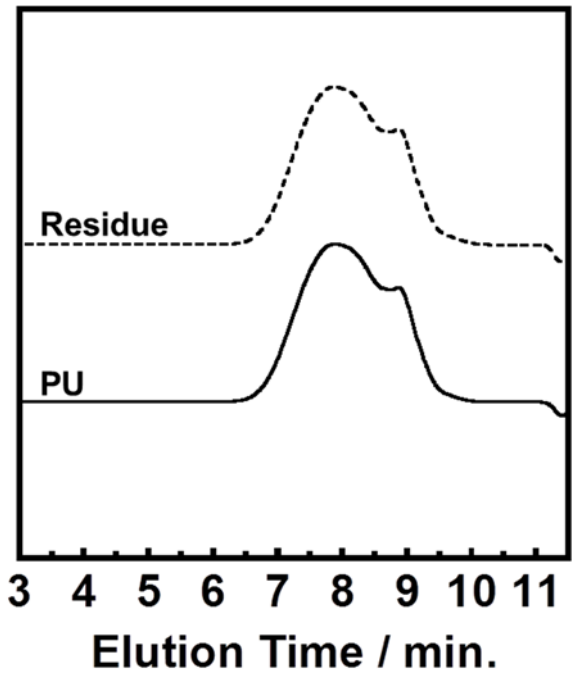


Figure S4. Gel permeation chromatography (GPC) profiles of PU (solid line) and insoluble residual solid (dashed line). DMF was used as the eluent.

The GPC profiles of both samples were almost same.

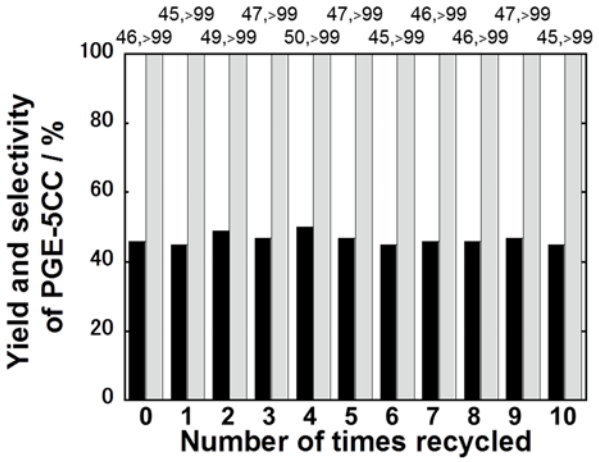


Figure S5. Catalyst recycling experiments. Left and right columns are yield and selectivity for PGE-5CC, respectively. Conditions; 150 °C, 9 MPa CO_2, 6h, $[\text{urethane group}]_0$ / $[\text{PGE}]_0$ = 1.0.

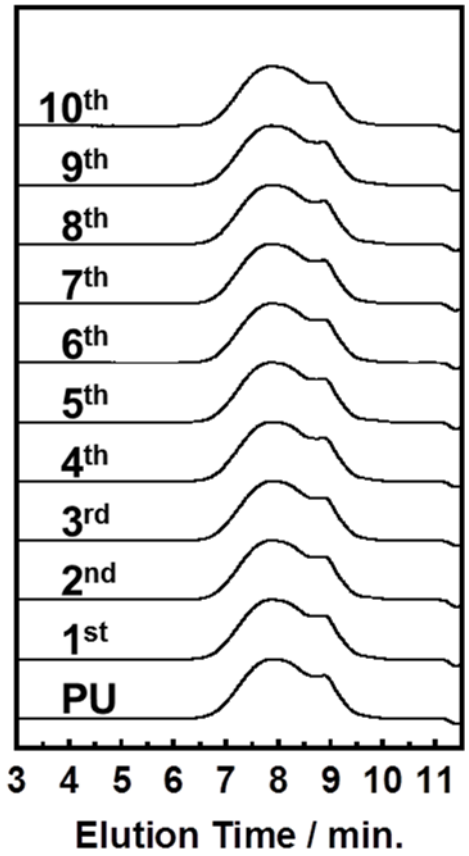


Figure S6. Gel permeation chromatography (GPC) profiles of PU and insoluble residual solid from recycled experiments. DMF was used as the eluent.

The GPC profiles in the recycled experiments were almost same.

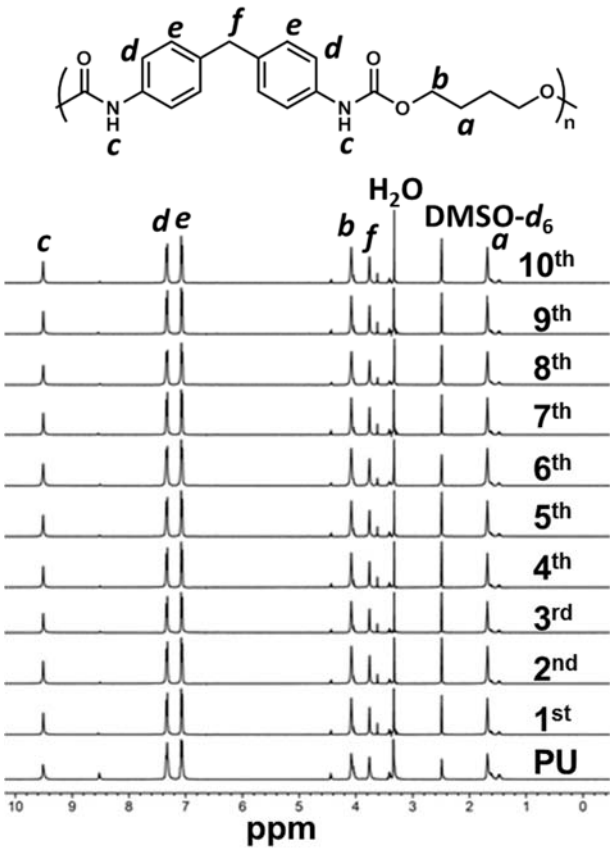


Figure S7. ^{1}H-NMR (DMSO-d_6) spectra of PU and insoluble residual solid obtained by filtration from recycled (1st - 10th) experiments.

The NMR spectra in the recycled experiments were almost same.

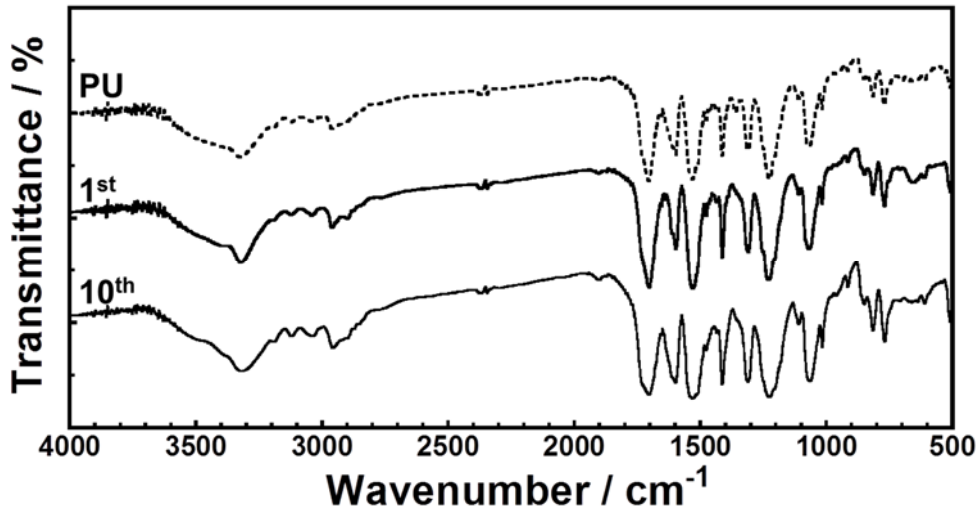


Figure S8. FT-IR spectra of PU (dotted line) and insoluble residual solid obtained by filtration from recycled (1st and 10th) experiments (solid line).

The FT-IR spectra in the recycled experiments were almost same.

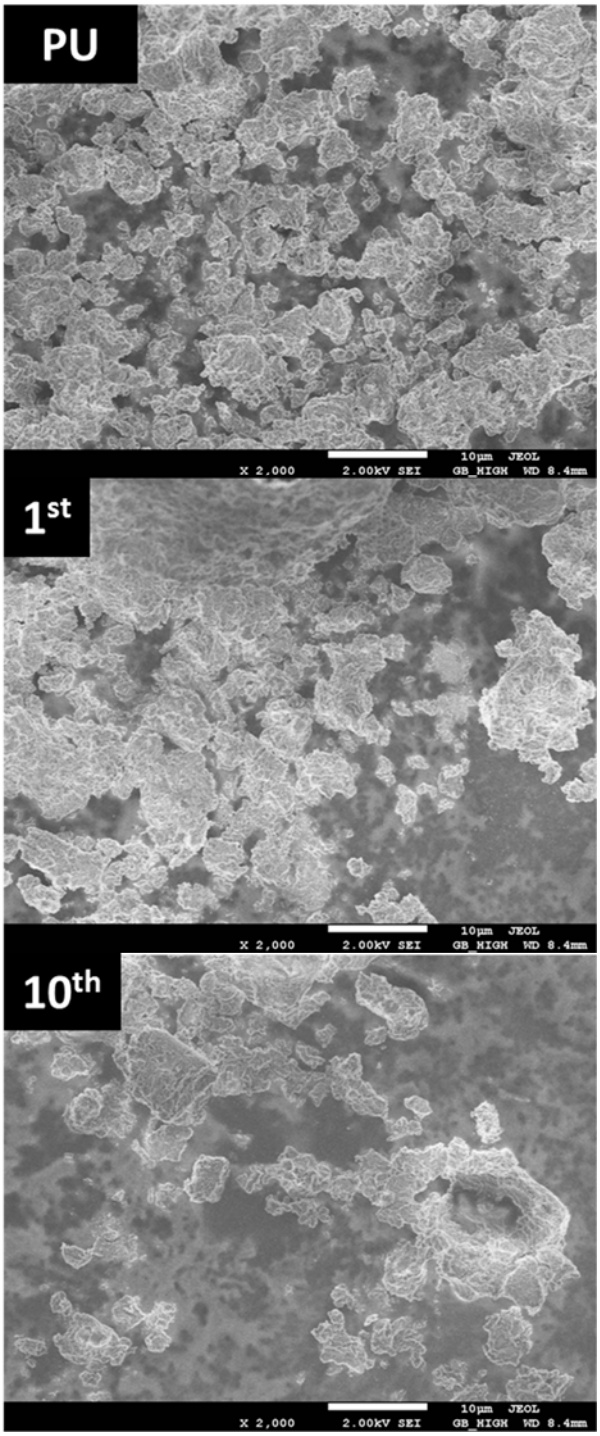


Figure S9. SEM images of PU and insoluble residual solid obtained by filtration from recycled (1st and 10th) experiments.

The morphologies of the PU samples in the recycled experiments were almost same.

Table S1. M_n, M_w, and $Đ$ (M_w/M_n) of PU and insoluble residual solid (residue).

	M_n /10^4	M_w /10^4	$Đ$
PU	4.1	6.3	1.5
Residue	4.2	5.8	1.4

M_n: number- average molecular weight; M_w: weight- average molecular weight; $Đ$: dispersity, defined as (M_w/M_n).

Table S2. Effects of the reaction conditions on the synthesis of PGE-5CC.

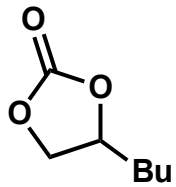
Entry	Temp. / °C	Time / h	Pressure / MPa	Isolated yield of PGE-5CC (selectivity) / %[a]
1	150	3	9.0	38(>99)
2	150	6	9.0	46(>99)
3	150	16	9.0	79(>99)
4	150	24	9.0	92(>99)
5	150	48	9.0	quant.(>99)
6	150	6	2.0	24(>99)
7	150	6	4.9	42(>99)
8	150	6	7.0	48(>99)
9	120	16	9.0	17(>99)
10	180	16	9.0	90(91)

Condition: molar ratio of [urethane group of PU]$_0$/[PGE]$_0$ = 1.0.
[a]Selectivity for PGE-5CC, in parenthesis, was determined from the ^{1}H-NMR spectrum of an aliquot of the reaction mixture.

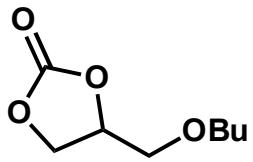
Table S3. Weights of PU and used-PU in the recycled experiment.

Number of times recycled	Weight of PU / g
0	0.85
1st	0.84
2nd	0.84
3rd	0.84
4th	0.84
5th	0.83
6th	0.83
7th	0.83
8th	0.83
9th	0.82
10th	0.82

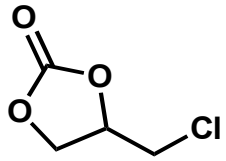
Molar ratio of [urethane group of PU]$_0$/[PGE]$_0$ = 1.0. The results were shown in **Figure S5**.



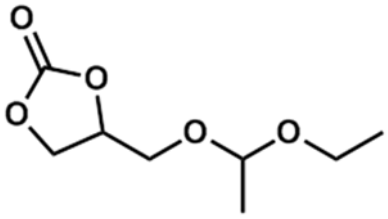
4-butyl-1,3-dioxolan-2-one (5CC-1)[1)]: Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.70–4.67 (m, 1H), 4.51–4.47 (t, J = 8.4 Hz, 1H), 4.06–4.02 (dd, J = 7.6, 8.4 Hz, 1H), 1.82–1.77 (m, 2H), 1.45–1.30 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ155.0, 76.9, 69.3, 33.4, 27.5, 23.7, 13.6.



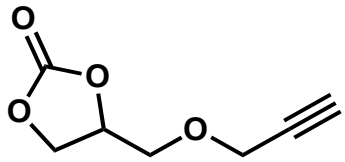
4-(butoxymethyl)-1,3-dioxolan-2-one (5CC-2)[1)]: Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ4.83–4.76 (m, 1H), 4.55–4.47 (dd, J = 8.4, 8.2 Hz, 1H), 4.39 (dd, J = 8.2, 6.3 Hz, 1H), 3.73–3.69 (dd, J = 11.6, 3.2 Hz, 1H), 3.55-3.44 (m, 1H), 3.41–3.38 (t, J = 6.0 Hz, 2H), 1.60–1.54 (m, 2H), 1.42–1.33 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ155.0, 75.1, 71.5, 69.5, 66.1, 31.3, 18.9, 13.6.



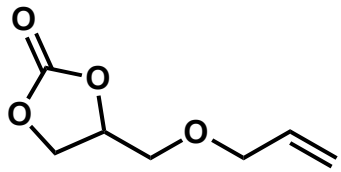
4-(chloromethyl)-1,3-dioxolan-2-one (5CC-3)[2)]: Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.01–4.93 (m, 1H), 4.59 (dd, J = 5.9, 8.9 Hz, 1H), 4.41 (dd, J = 5.9, 8.8 Hz, 1H), 3.81–3.69 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.2, 74.3, 66.9, 43.7.



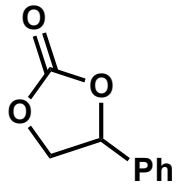
4-((1-ethoxyethoxy)methyl)-1,3-dioxolan-2-one (5CC-4): Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ4.90–4.85 (m, 1H), 4.81–4.76 (m, 1H), 4.56–4.51 (m, 1H), 4.44–4.36 (m, 1H), 3.85–3.76 (m, 1H), 3.73–3.59 (m, 2H), 3.54–3.47 (m, 1H), 1.32 (d, J = 5.3 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ154.8, 99.42, 74.8, 66.0, 63.1, 60.9, 19.4, 14.9.



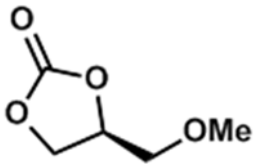
4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (5CC-5)[1)]: Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.89–4.86 (m, 1H), 4.54–4.50 (t, J = 1H), 4.43–4.39 (dd, J = 6.0 Hz, 8.4, 1H), 4.27–4.18 (m, 2H), 3.79–3.76 (m,2H), 2.51 (t, J = 2.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ155.7, 78.6, 75.1, 74.2, 69.8, 64.9, 59.2.



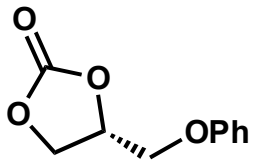
4-((allyloxy)methyl)-1,3dioxolan-2-one (5CC-6)[2)]: Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ5.96–5.83 (m, 1H), 5.31–5.18 (m, 2H), 4.87–4.82 (m, 1H), 4.54–4.50 (t, J = 8.4 Hz, 1H), 4.42–4.38 (dd, J = 6.0 Hz, 8.4 Hz, 1H), 4.09–4.02 (m, 2H), 3.76–3.60 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.0, 133.7, 117.8, 75.1, 72.6, 68.9, 66.3.



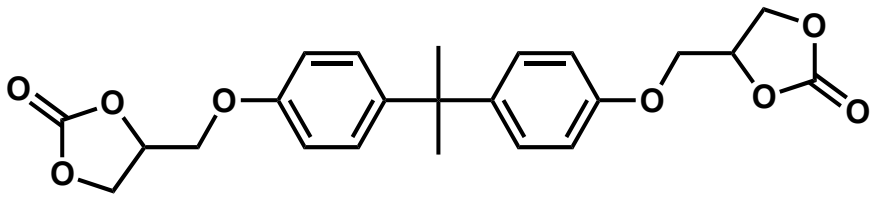
4-Phenyl-1,3-dioxolan-2-one (5CC-7)[1)]: White Solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.48–7.35 (m, 5H), 5.68 (dd, J = 8.3, 8.2 Hz, 1H), 4.80 (dd, J = 8.0, 8.3 Hz, 1H), 4.35 (dd, J = 7.6, 8.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ154.8, 135.7, 129.7, 129.1, 125.8, 77.9, 71.1.



(*S*)-4-(methoxymethyl)-1,3-dioxolan-2-one (5CC-8)[3)]: White Solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ4.86–4.79 (m, 1H), 4.51 (t, J = 8.4 Hz, 1H), 4.39 (dd, J = 6.1, 8.3 Hz,1H), 3.66 (dd, J = 3.7, 11.0 Hz, 1H), 3.57 (dd, J = 3.8, 11.0 Hz, 1H), 3.43 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ154.9, 74.9, 71.4, 66.1, 59.5. $[a]_D^{20}$ = -37 (c = 1.0, EtOH) [lit.3 $[a]_D^{20}$ = -44 ~ -47 (neat, >98% ee (*S*))].



(*R*)-4-(phenoxymethyl)-1,3-dioxolan-2-one (5CC-9)[4)]: White Solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ7.31 (t, J = 8.0 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 5.06–5.00 (m, 1H), 4.61 (t, J = 8.41H), 4.54 (dd, J = 6.0, 8.5 Hz, 1H), 4.24 (dd, J = 4.3, 10.6 Hz, 1H), 4.15 (dd, J = 3.6, 10.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$)157.8, 154.8, 129.7, 121.9, 114.6, 74.3, 66.9, 66.2.
. HPLC analysis: Daicel Chiralcel OD-3, haxane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 39.1 min (minor) and 52.2 min (major).$[a]_D^{21}$ = +18.0 (c = 1.0, EtOH) [lit.4 $[a]_D^{20}$ = +18.3 (c = 1.2, EtOH; 99% ee (*R*))].



4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (5CC-10)[2)]: White solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.14 (d, J = 8.8 Hz, 4H), 6.81 (d, J = 8.8 Hz, 4H), 5.04–4.98 (m, 2H), 4.60 (t, J = 8.5 Hz, 2H), 4.51 (dd, J = 5.9, 8.5 Hz, 2H), 4.21 (dd, 2H, J = 4.3, 10.6 Hz), 4.12 (dd, J = 3.6, 10.6 Hz, 2H), 1.63 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ155.7, 1554.8, 143.3, 127.9, 114.0, 74.8, 67.4, 66.2, 41.2, 30.1.

Reference:
1) Fujihara, T.; Inokuchi, M.; Mizoe, T.; Nogi, K.; Terao, J.; Tsuji, Y. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide Catalyzed by $MgCl_2$ *Chem. Lett.*, **2017**, 46, 7, 968-969, https://doi.org/10.1246/cl.170252.
2) Rostami, A.; Mahmoodabadi, M.; Ebrahimi, A. H.; Khosravi, H.; Al-Harrasi, A. An Electrostatically Enhanced Phenol as a Simple and Efficient Bifunctional Organocatalyst for Carbon Dioxide Fixation *ChemSusChem*, **2018**, 11, 4264–4268, DOI : 10.1002/cssc.201802028.
3) Authentic sample available, https://www.tcichemicals.com/eshop/en/jp/commodity/M1456/ (accessed 2020/02/07)
4) Kaneko, S.; Shirakawa, S. Potassium Iodide−Tetraethylene Glycol Complex as a Practical Catalyst for CO_2 Fixation Reactions with Epoxides under Mild Conditions *ACS Sustain. Chem. Eng.*, **2017**, 5, 2836–2840, DOI: https://doi.org/10.1021/acssuschemeng.7b00324