Electronic Supplementary Information (ESI)

Direct synthesis of polycarbonate diols from atmospheric flow CO_2 and diols without using dehydrating agents

Yu Gu,[1] Masazumi Tamura,[2]*, Yoshinao Nakagawa,[1] Kenji Nakao,[3] Kimihito Suzuki,[3] Keiichi Tomishige,[1]*

1. Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan
2. Research Center for Artificial Photosynthesis, The Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan
3. Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511 Japan

*E-mail: mtamura@osaka-cu.ac.jp (M.T.), tomi@erec.che.tohoku.ac.jp (K.T.)

Detailed Methods

1. Sample analysis

The collected liquid samples were analysed by a gas chromatograph (Shimadzu, GC-2014) equipped with an FID detector and a CP-Sil5 CB column (Agilent, length = 50 m, i.d. = 0.25 mm, film thickness = 0.25 μm). The sample from the flask was also analysed by size exclusion chromatography, SEC (Shimadzu, Prominence HPLC System), equipped with an RI detector (RID-10A) and an SEC column KF-803L (Shodex, particle size = 6 μm, 8.0 mm×300 mm, flow rate = 1.0 mL min^{-1}) using THF (FUJIFILM Wako Pure Chemical Corporation, purity > 99.5%) as eluent for determining the M_n and M_w/M_n of the samples (the calibration curve with 7 points was obtained by using polystyrene as standards). The qualitative analysis of the products was conducted by a gas chromatograph equipped with a quadrupole mass spectrometer (Shimadzu, GCMS-QP2010 Ultra) using the same capillary column.

2. Catalyst characterization

The surface areas of the used catalysts were measured by using Brunauer-Emmett-Teller (BET) technique (N_2 adsorption) with Gemini VII (Micromeritics). X-ray diffraction (XRD) patterns were recorded using MiniFlex 600 with Cu Kα (40 kV, 15 mA) radiation.

3. Analysis of water amount in samples

1 mL reaction mixture was collected at the reaction temperature from the flask by using a syringe and then was injected into a Karl-Fischer coulometer (899 Coulometer, Metrohm AG) to determine the water content. In the case of the reaction carried out using an autoclave reactor, the sample was collected from the autoclave after it was cooled to 333 K and purged.

4. Solubility measurement

1,6-Hexanediol was added to a solvent in 1:1 volume ratio under 333 K, which is slightly higher than the melting point of 1,6-hexanediol (315 K). The sample was shaken for several seconds and put into an isothermal water bath (298 K) for 0.5 h. The precipitated 1,6-hexanediol under 298 K was filtered out, and the solution was then put in the isothermal water bath (298 K) for another 0.5 h to make sure there was no more precipitation of 1,6-hexanediol. The solution was diluted with ethanol in equal volume, and the amount of dissolved 1,6-hexanediol in the solvent was determined by gas chromatography using an external standard method. The solubility is defined as miscible (∞) if all 1,6-hexanediol can be dissolved in a solvent.

The solubility of a solvent in water was measured similarly. A solvent was added to water in 1:1 volume ratio. The sample was shaken for several seconds and kept still until the liquid phase(s) became clear. The water phase was then collected and the amount of dissolved organic solvent in water was determined by gas chromatography using an external standard method.

5. Experimental method to determine the water affinity of solvents

The water affinity of solvents is used to show the ability of solvents to retain water under standard reaction conditions. A quantity of 0.10 g of distilled water was added to the substrates (CeO_2 0.10 g, 1,6-hexanediol 2.0 g, solvent 3 g) in advance (water content: 20,000 ppm). The obtained mixture was then introduced with CO_2 flow (200 mL min^{-1}), and heated in a 483 K isothermal oil bath for 10 min (the temperature of the reaction mixture in the reactor reached 473 K in 10 minutes). One mL of the heated sample was collected and injected into a Karl-Fischer coulometer to measure how much water was retained in the mixture. The concentration of the water retained in the heated sample with different solvents is defined as the water affinity of solvents.

6. Procedure of catalyst reusability test

The solid catalyst in the collected mixture diluted with THF (40 g) was separated by centrifugation and washed with THF (30 g) 2 times and methanol (30 g) for 1 time to remove organic compounds on the surface of the catalyst. The washed catalyst was dried in an oven at 383 K in air for one night and then used for the next run under the same reaction condition as the first run. Several batches were carried out in parallel, and the catalyst collected from the parallel reactions was used to compensate for the catalyst loss in the procedure of reuse (the loss was about 15 wt%).

7. Separation of the produced polymer at 96 h reaction

The collected reaction mixture was filtered to remove the solid CeO_2 catalyst, and the received filtrate was treated by vacuum evaporation to prepare a concentrated solution of the products. The concentrated solution was then added to 50 mL methanol dropwise and cooled down to 255 K. The produced polymer precipitated from the cold methanol as a white solid and was separated by centrifugation. The white solid was washed with fresh methanol 5-6 times until there were no reaction solvents (triglyme and diphenyl ether) detected in the washing solution (determined by GC-FID). Finally, the separated white solid was placed in a vacuum bell jar to remove the washing solvent (methanol).

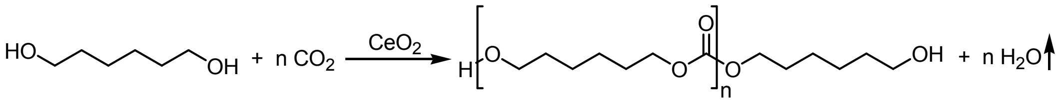
8. NMR analysis

The separated polymer was dissolved in $CDCl_3$ (Kanto Chemical, 0.03 vol% TMS, deuteration degree > 99.8%, stabilized with silver) to form a 10wt% solution, which was used as the sample for NMR analysis carried out on Bruker, AV400.

9. MALDI-TOF mass analysis

The separated polymer was dissolved in THF at concentration of 10 mg mL^{-1}. 1,8,9-Trihydroxyanthracene (Tokyo Chemical Industry, purity > 95.0%) was used as matrix, and sodium trifluoroacetate (Tokyo Chemical Industry, purity > 98.0%) was used as ionization agent. The matrix and cationizing agent were also dissolved separately in THF at the concentration of 10 mg mL^{-1}. The polymer solution, dissolved matrix, and cationizing agent were mixed in a 1:1:2 ratio, and the mixture was spotted on the MALDI plate and left to dry. The sample was then analysed by MALDI-TOF mass (AB SCIEX, TOF/TOF 5800) in reflector mode.

10. Quantitative analysis



Dimer: n=1, Polymer: n>1

Amounts of the unreacted diol and the produced dimer were determined by gas chromatography using an internal standard method. Amount of the produced trimer was determined by SEC-HPLC using the produced dimer as an internal standard substance. The unreacted diol was collected from both the flask and the trap on the outlet of the reactor (Fig. S2).

Conversion of the diol and yield of the dimer were calculated by the following equations:

Conversion (%) = [1- Unreacted diol (mmol)] / [Input amount of diol (mmol)] × *100*

Yield of dimer (%) = 2 × *[Amount of dimer diol (mmol)] / [Input amount of diol (mmol)]* × *100*

Yield of polymer was calculated by the following equations:

When the conversion was below 20%, and the produced polymer was mainly the trimer. Yield of the trimer was calculated by SEC-HPLC using the peak sensitivity of dimer which was determined by GC and SEC-HPLC analyses. Hence, the yield of polymer below 20% conversion was calculated by the following equation:

Yield of polymer (%) (≤20% conversion) = 3 × [Amount of trimer (mmol)] / [Input amount of diol (mmol)] × 100

When the conversion was above 20%, the composition of the produced polymers became more complicated, and the estimation of yield of all produced polymers by SEC-HPLC analysis was difficult. Hence, the yield of polymer above 20% conversion was calculated in another way as below:

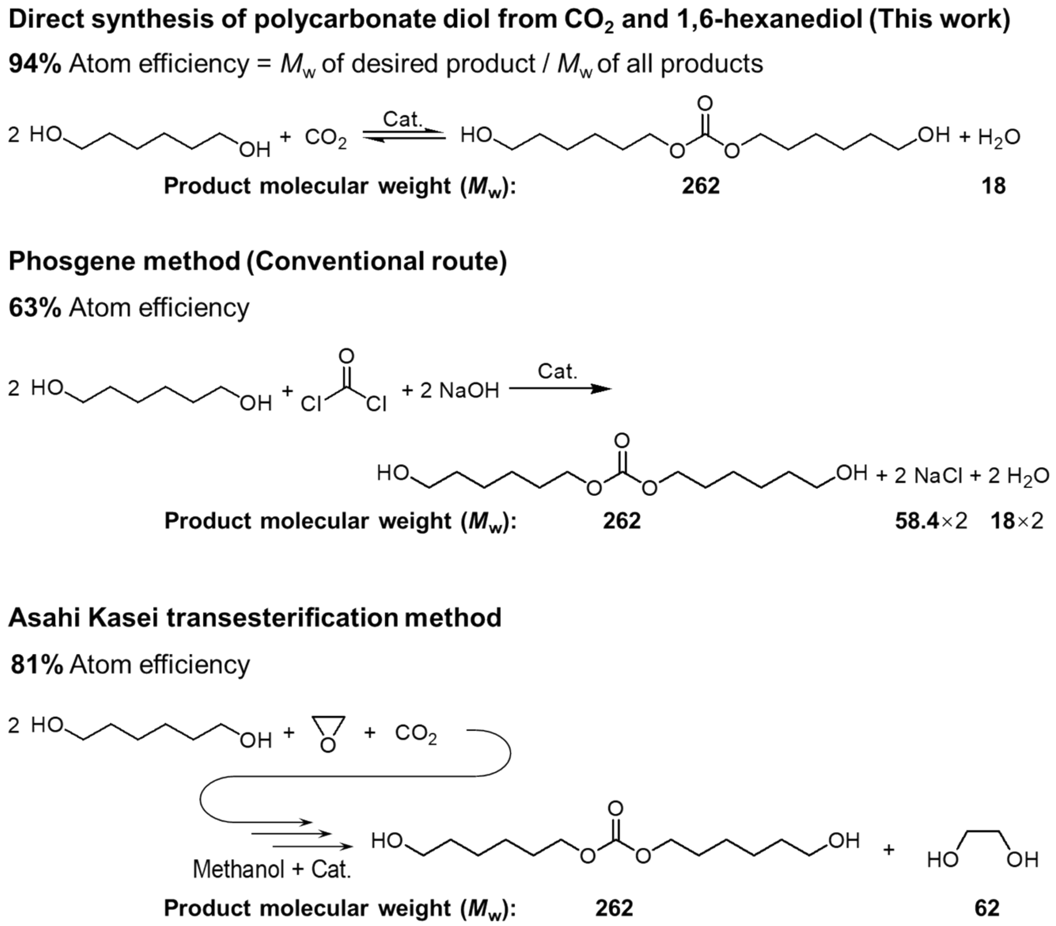
Yield of polymer (%) (>20% conversion) = Conversion (%) – [Yield of dimer (%)]

Selectivity of the product was calculated by the following equation:

Selectivity (%) = (Yield / Conversion) × 100

Material balance of the diol was calculated by the following equation:

Diol balance (%) (≤20% conversion) = {[Amount of unreacted diol in flask (mmol)] + 2 × [Amount of dimer (mmol)] + 3 × [Amount of trimer (mmol)]} / [Input amount of diol (mmol)] × 100



Direct synthesis of polycarbonate diol from CO_2 and 1,6-hexanediol (This work)

94% Atom efficiency = M_w of desired product / M_w of all products

Phosgene method (Conventional route)

63% Atom efficiency

Asahi Kasei transesterification method

81% Atom efficiency

Fig. S1 Atom efficiency of the three routes in the case of bis(6-hydroxyhexyl) carbonate synthesis from 1,6-hexanediol and CO_2

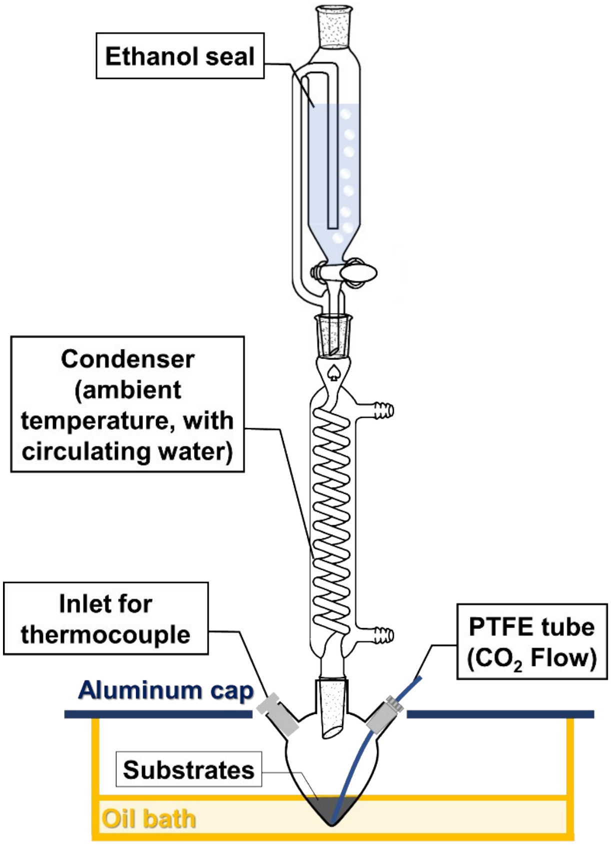


Fig. S2 Illustration of the CO_2 flow semi-batch reactor. A pear-shaped flask was used to avoid deposition of the solid catalyst with CO_2 bubbling in from the bottom.

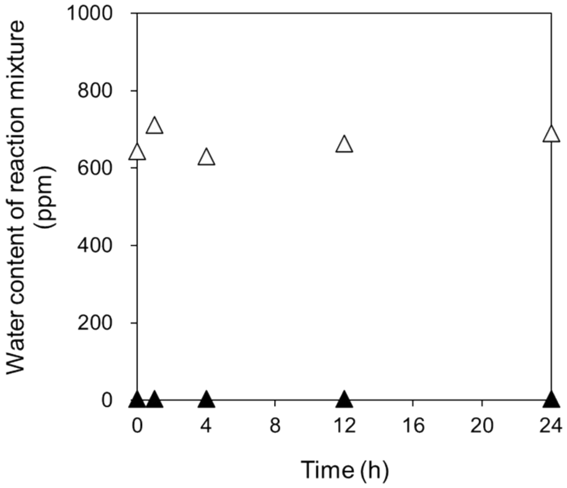


Fig. S3 Water content of the reaction mixture from the two different reactors. (Black triangle, CO_2 flow semi-batch reactor; white triangle, Sealed-batch reactor).

Reaction conditions of CO_2 flow semi-batch reactor: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 3 g, 473 K, CO_2 flow rate 200 mL min^{-1}; Reaction conditions of sealed-batch reactor: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 3 g, 473 K, CO_2 7.5 MPa.

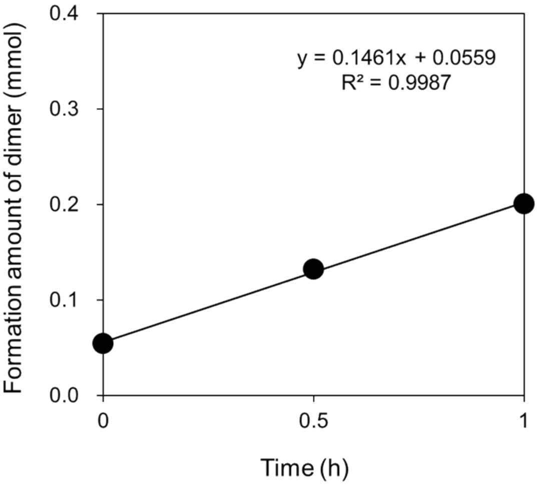


Fig. S4 The initial rate of bis(6-hydroxyhexyl) carbonate formation over CeO_2.

Reaction conditions: CeO_2 0.01 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 2 g, diphenyl ether 3 g, CO_2 flow rate 200 mL min^{-1}, 483 K, 0-1 h. Dimer selectivity was above 99% under this reaction conditions.

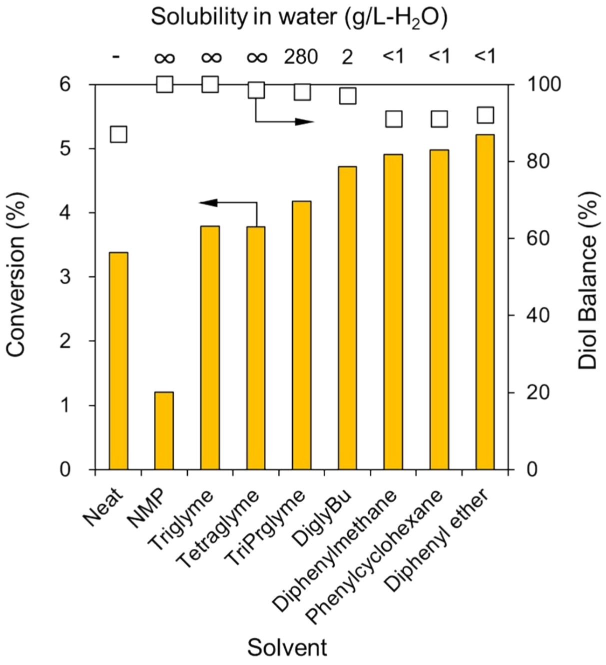
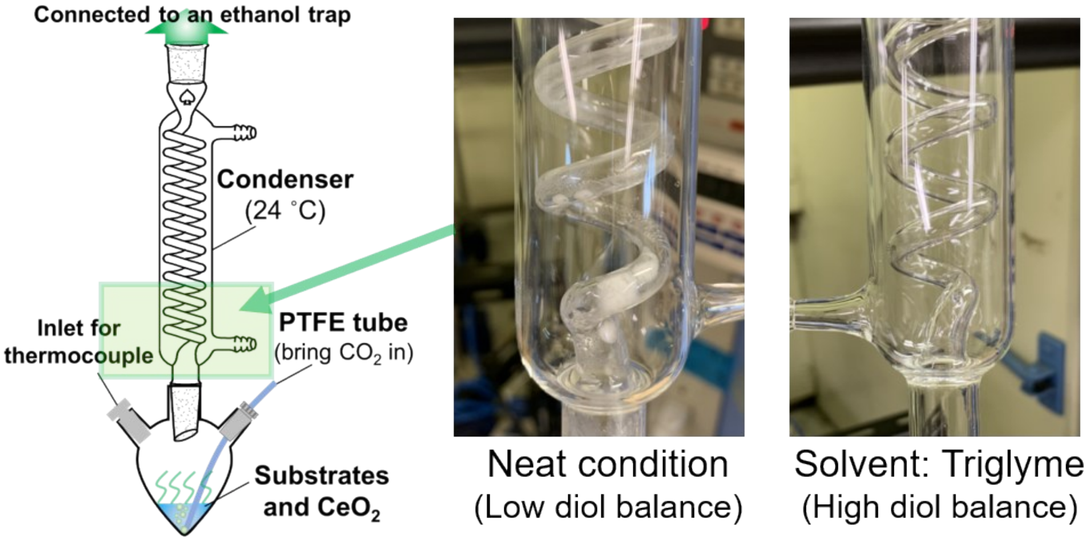


Fig. S5 Solvent effect in the reaction of CO_2 and 1,6-hexanediol over CeO_2. ○, diol balance; bar, conversion. Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), solvent 0 (neat) or 3 g, CO_2 flow rate 200 mL min^{-1}, 473 K, 1 h.



Neat condition
(Low diol balance)

Solvent: Triglyme
(High diol balance)

Fig. S6 Photos of the condenser after the reaction (the white solid in the condenser is 1,6-hexanediol). Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 0 (neat) or 3 g, CO_2 flow rate 200 mL min^{-1}, 473 K, 1 h.

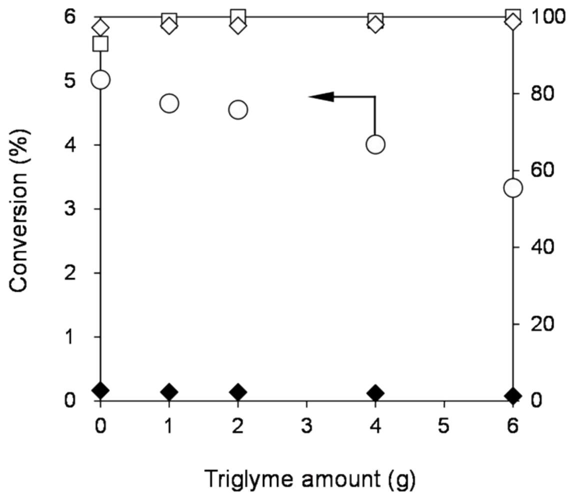


Fig. S7 Effect of triglyme amount in the dual-solvents system. Marks in the figure: ○, conversion; ⭘, diol balance; ❋, dimer selectivity; ◆, polymer selectivity. Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 0–6 g, diphenyl ether 3 g, CO_2 flow rate 200 mL min^{-1}, 473 K, 1 h.

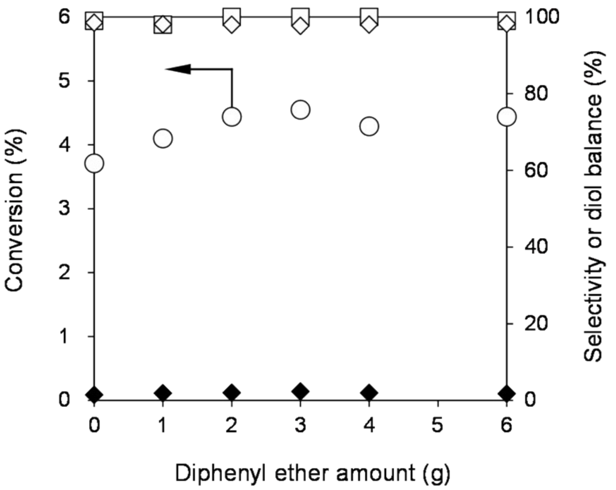
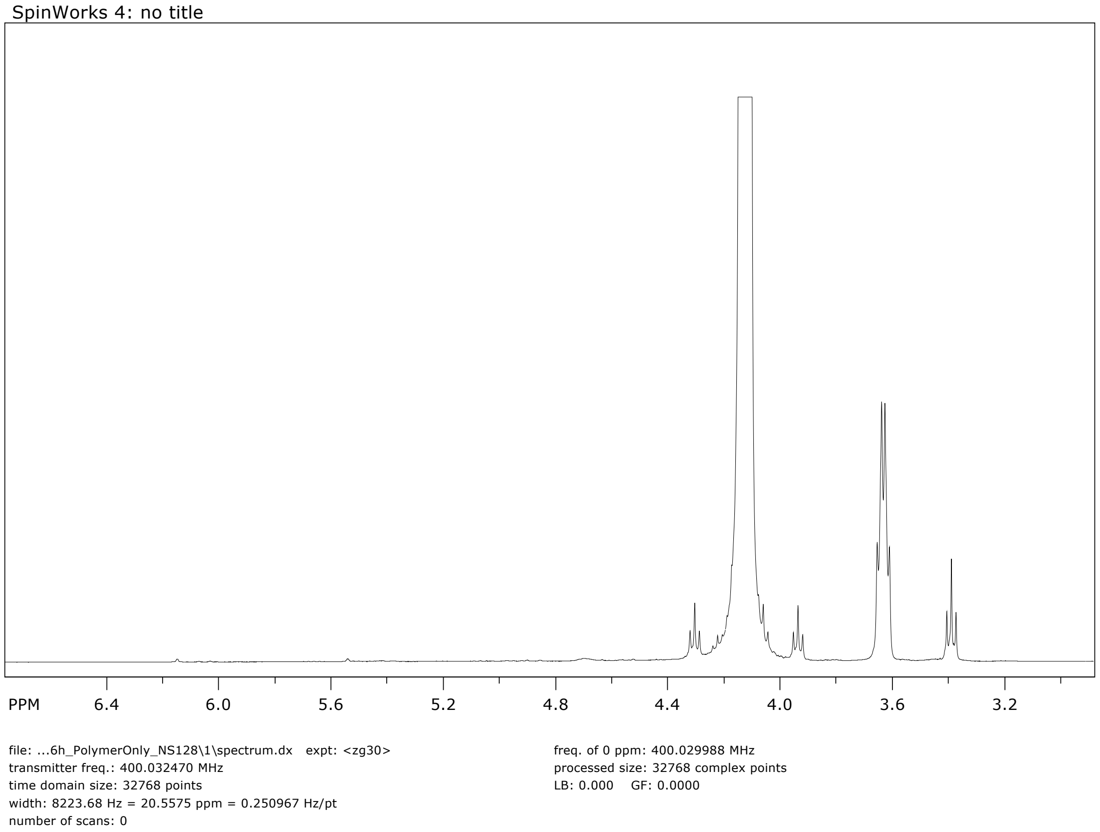


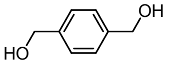
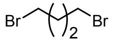
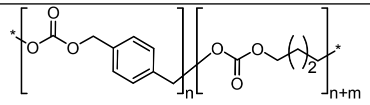
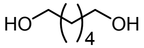
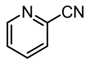
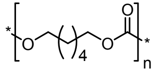
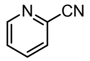
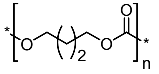
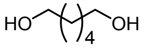
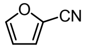
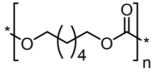
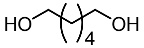
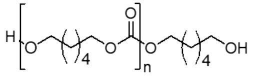
Fig. S8 Effect of diphenyl ether amount in the dual-solvents system. Marks in the figure: ○, conversion; ◉, diol balance; ❋, dimer selectivity; ◆, polymer selectivity. Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 2 g, diphenyl ether 0–6 g, CO_2 flow rate 200 mL min^{-1}, 473 K, 1 h.



```
file: ...6h_PolymerOnly_NS128\1\spectrum.dx   expt: <zg30>        freq. of 0 ppm: 400.029988 MHz
transmitter freq.: 400.032470 MHz                                processed size: 32768 complex points
time domain size: 32768 points                                   LB: 0.000    GF: 0.0000
width: 8223.68 Hz = 20.5575 ppm = 0.250967 Hz/pt
number of scans: 0
```

Fig. S9 ^{1}H-NMR spectrum of polycarbonate diol produced in 96 h (enlarged version of Fig. 6e)

Table S1 Previously reported phosgene-free synthesis of polycarbonates from CO_2 and diols

Entry	Diol	Co-reactant	Catalyst	P_{CO2} (MPa)	Temp . (K)	Time (h)	Conv. (%)	M_n (g mol^{-1}), M_w/M_n^{a}	Product	Ref.
1		 1.05 equiv.	Cs_2CO_3	1.0	373	48	97	22000, 3.6	 Polycarbonate	[S1]
2		 10 equiv.	CeO_2	5.0 (at r.t.)	403	24	99	1080, 1.3	 Polycarbonate	[S2]
3		 5 equiv.	CeO_2 nanorod	5.0 (at r.t.)	423	8	97	1030, 1.4	 Polycarbonate	[S3]
4		 20 equiv.	CeO_2	5.0 (at r.t.)	403	24	>99	5000, 1.5	 Polycarbonate	[S4]
5		-	CeO_2	0.1 (200 mL min^{-1} flow)	483	96	95	3500, 2.4	 Polycarbonate diol	This work

^{a}Determined by SEC.

Table S2 Time-course with sealed-batch reactor under high CO_2 pressure (7.5 MPa) (Detailed data of Fig. 2b)

Entry	Time (h)	Conversion (%)	Yield (%)			Water content (mmol)
			Dimer	Polymer	Others[a]	
1	0	0.75	0.75	<0.01	<0.01	0.18
2	1	0.90	0.90	<0.01	<0.01	0.20
3	4	0.85	0.85	<0.01	<0.01	0.18
4	12	0.80	0.74	<0.01	0.06	0.18
5	24	0.91	0.69	<0.01	0.22	0.19

Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 3 g, 473 K, CO_2 7.5 MPa. [a]Including 6-hydroxyhexanoic acid 6-hydroxyhexyl ester and bis(6-hydroxyhexyl) ether.

Table S3 Detailed data of the time-course with sealed-batch reactor under atmospheric CO_2 (0.1 MPa)

Entry	Time (h)	Conversion (%)	Yield (%)		
			Dimer	Polymer	Others
1	0	<0.01	<0.01	<0.01	<0.01
2	1	<0.01	<0.01	<0.01	<0.01
3	4	<0.01	<0.01	<0.01	<0.01
4	12	<0.01	<0.01	<0.01	<0.01
5	24	<0.01	<0.01	<0.01	<0.01

Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 3 g, 473 K, CO_2 0.1 MPa.

Table S4 Reaction of flow CO_2 and 1,6-hexanediol over various solid oxides

Entry	Catalyst	S_{BET} (m^2 g^{-1})	Conv. (%)	Selectivity (%)		
				Dimer	Polymer	Others
1	-	-	-	-	-	-
2	CeO_2	84	17	89	11	<1
3	γ-Al_2O_3	95	40	<1	<1	>99
4	SiO_2-Al_2O_3	405	32	<1	<1	>99
5	SiO_2	453	<1	-	-	-
6	MgO	38	<1	-	-	-
7	ZrO_2	45	<1	-	-	-
8	TiO_2	55	<1	-	-	-
9	ZnO	12	<1	-	-	-
10	Y_2O_3	40	<1	-	-	-
11	La_2O_3	107	<1	-	-	-
12	Dy_2O_3	58	<1	-	-	-
13	Gd_2O_3	60	<1	-	-	-
14	Eu_2O_3	69	<1	-	-	-
15	Sm_2O_3	79	<1	-	-	-
16	Pr_6O_{11}	105	<1	-	-	-

Reaction conditions: Solid oxide 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), CO_2 flow rate 200 mL min^{-1}, triglyme 2 g, diphenyl ether 3 g, 483 K, 4 h. Others in the case of γ-Al_2O_3 and SiO_2-Al_2O_3 are linear ether from bimolecular dehydration of 1,6-hexanediol and cyclic ether, 5-hexen-1-ol and its isomers from unimolecular dehydration of 1,6-hexanediol.

Table S5 Solubility of 1,6-hexanediol in various organic solvents under 298 K

Solvent	Solubility of 1,6-hexanediol under 298 K (g/L-solvent)
H_2O	Miscible
N-Methyl-2-pyrrolidone (NMP)	Miscible
Triethylene glycol dimethyl ether (Triglyme)	620
Tetraethylene glycol dimethyl ether (Tetraglyme)	210
Tripropylene glycol dimethyl ether (TriPrglyme, isomer mixture)	90
Diethylene glycol dibutyl ether (DiglyBu)	30
Diphenylmethane	3
Phenylcyclohexane	2
Diphenyl ether	2

Table S6 Effect of mixed gas of CO_2 and N_2 (Detailed data of Fig. 4)

Flow rate (mL min^{-1})			Conv. (%)	Selectivity (%)		
Total	CO_2	N_2		Dimer	Polymer	Others
70	70	0	2.4	>99	<1	<1
100	70	30	2.5	>99	<1	<1
150	70	80	2.5	>99	<1	<1
200	70	130	2.6	>99	<1	<1
250	70	180	2.6	>99	<1	<1

Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 2 g, diphenyl ether 3 g, CO_2 flow rate 70 mL min^{-1}, N_2 flow rate 0-180 mL min^{-1}.

Table S7 Effect of pure CO_2 flow (Detailed data of Fig. 4)

CO_2 Flow rate (mL min^{-1})	Conv. (%)	Selectivity (%)		
		Dimer	Polymer	Others
70	2.4	>99	<1	<1
100	2.9	99	1	<1
150	4.0	98	2	<1
200	5.1	97	3	<1
250	5.3	97	3	<1

Reaction conditions: CeO_2 0.10 g, 1,6-hexanediol 2.0 g (17 mmol), triglyme 2 g, diphenyl ether 3 g, CO_2 flow rate 70-250 mL min^{-1}.

Reference

S1 Z. Chen, N. Hadjichristidis, X. Feng and Y. Gnanou, *Polym. Chem.,* 2016, **7**, 4944–4952.
S2 M. Tamura, K. Ito, M. Honda, Y. Nakagawa, H. Sugimoto and K. Tomishige, *Sci. Rep.*, 2016, **6**, 24038.
S3 Z.-J. Gong, Y.-R. Li, H.-L. Wu, S.D. Lin and W.-Y. Yu, *Appl. Catal. B*, 2020, **265**, 118524.
S4 Y. Gu, K. Matsuda, A. Nakayama, M. Tamura, Y. Nakagawa and K. Tomishige, *ACS Sustainable Chem. Eng.*, 2019, **7**, 6304–6315.