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Direct Copolymerization of CO_2 and Diols

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Direct polymerization of CO_2 and diols is promising as a simple and environmental-benign method in place of conventional processes using high-cost and/or hazardous reagents such as phosgene, carbon monoxide and epoxides, however, there are no reports on the direct method due to the inertness of CO_2 and severe equilibrium limitation of the reaction. Herein, we firstly substantiate the direct copolymerization of CO_2 and diols using CeO_2 catalyst and 2-cyanopyridine promotor, providing the alternating cooligomers in high diol-based yield (up to 99%) and selectivity (up to >99%). This catalyst system is applicable to various diols including linear C4-C10 α,ω-diols to provide high yields of the corresponding cooligomers, which cannot be obtained by well-known methods such as copolymerization of CO_2 and cyclic ethers and ring-opening polymerization of cyclic carbonates. This process provides us a facile synthesis method for versatile polycarbonates from various diols and CO_2 owing to simplicity of diols modification.

Direct transformation of CO_2 to valuable chemicals is one of the hottest topics from the viewpoints of environmental and green chemistry[1–7]. Transformation of CO_2 can be mainly categorized into two methods, reductive transformation and non-reductive transformation[1,4,5]. The non-reductive transformation of CO_2 comprises the reactions of CO_2 with compounds having polar functional groups such as alcohols and amines, providing various important chemicals such as ureas, carbamates, carbonates and polycarbonates, and it is promising because of lower energy input compared with the reductive transformation. However, since CO_2 is very stable owing to the very strong double bond, an exquisite catalyst system to activate CO_2 and reagents is essential. Carbonic anhydrase is well-known as an ideal catalyst system for non-reductive transformation of CO_2, drastically accelerating the reaction of CO_2 and H_2O to bicarbonate and proton (~10^6-fold vs non-catalyst)[8–12]. In this catalyst system, Zn^{2+} ion and a histidine residue activate H_2O to generate reactive hydroxide species on Zn^{2+} ion (cooperation of Lewis acid and Lewis base), and CO_2 is guided near the hydroxide species by the hydrophobic pocket composed of three valine residues (substrate concentration), forming a configuration that is conductive to reaction. As for artificial catalysts, achieving the sufficient level comparable to enzymes is quite difficult due to the smaller size of the artificial catalysts than enzymes. Therefore, it is desirable to create exquisite and precise artificial catalysts that can simultaneously activate CO_2 and reagents in proximity of each other.

CeO_2 has been widely used in the fields of catalyst and biological chemistry because of its unique acid-base and redox properties[13,14], and has recently attracted much attention in liquid-phase organic syntheses at low temperature ($\leq 473\,K$)[15–21]. In particular, it has been reported that CeO_2 plays a crucial role in the catalytic non-reductive conversion of CO_2 to organic carbonates, carbamates and ureas using alcohols or amines[22–32], although these reactions have a common problem of the equilibrium limitation. Recently, we found that CeO_2-catalyzed dehydration condensation of alcohols and CO_2 in combination with CeO_2-catalyzed hydration of 2-cyanopyridine to picolinamide enabled the formation of the corresponding organic carbonates in high yields[33–35]. The methanol-based yield of DMC in the reaction of CH_3OH, CO_2 and 2-cyanopyridine reached 94% yield, while the equilibrium yield of DMC is below 1% in the reaction of CH_3OH and CO_2 without 2-cyanopyridine. This is the first report on stoichiometric transformation of alcohols with CO_2 to the corresponding carbonate. We also demonstrated that CO_2 can be strongly adsorbed and activated on acid-base sites of CeO_2[33–35] and that methanol can be activated cooperatively by both CeO_2 and 2-cyanopyridine at the interface between CeO_2 and 2-cyanopyridine[36], which has something common to the above enzyme catalyst system (mainly cooperation of Lewis acid and Lewis base,

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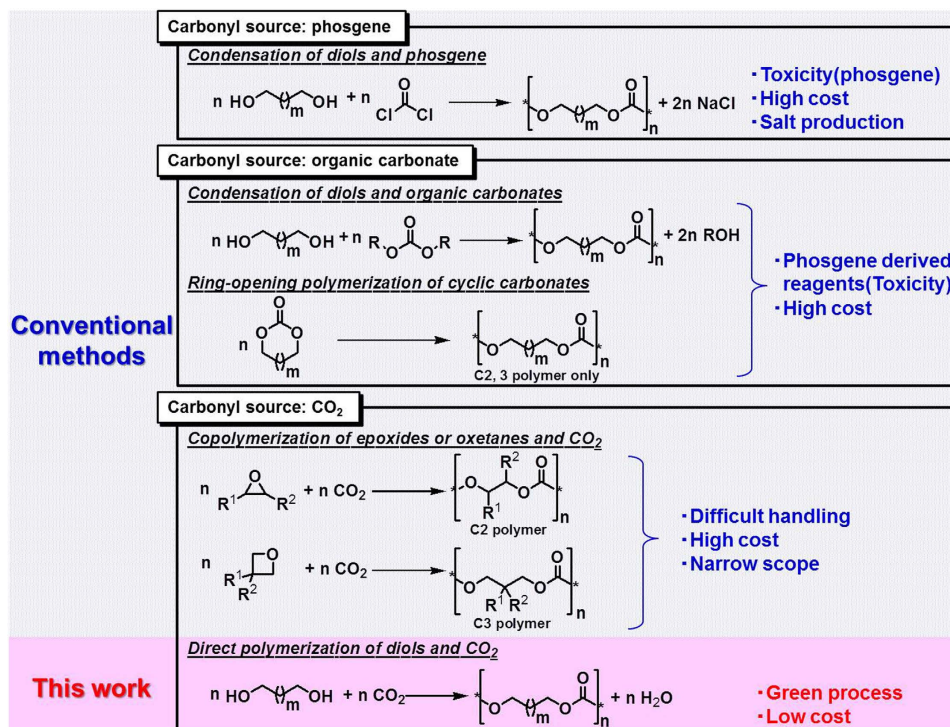
Figure 1. Synthesis methods of polycarbonates.

and substrate concentration). In addition, Urakawa and co-workers also applied this catalyst system to the DMC synthesis under a wide range of CO_2 pressure (1–30 MPa) in a fixed bed reactor, achieving higher reaction rates than that in batch operation[37]. These results inspired us to apply this catalyst system to the direct synthesis of polycarbonates from CO_2 and diols.

Polycarbonates has been commonly used as an engineering plastic, and the market size is 290 million ton/year in 2009 and expected to increase on average by about 4～6% each year to 2020[38,39]. Therefore, the polycarbonates are one of the most promising targets from CO_2, which will contribute to the incorporation of large amount of CO_2 into chemicals due to the large market size. Polycarbonates have been industrially produced by using phosgene as a carbonyl source, however, phosgene is highly toxic, and the process gives rise to a large amount of salts by neutralization. To overcome these drawbacks, processes using organic carbonates as a carbonyl source have been developed such as condensation of diols and organic carbonates[40–42] and ring-opening polymerization of cyclic carbonates[43–47] (Fig. 1). However, these processes have similar problems to the phosgene process because the organic carbonate substrates in these processes have been usually synthesized by the reaction of phosgene with the corresponding alcohols or epoxides, and an alternative environmental-benign synthesis process of the organic carbonates have not been established. As for processes using CO_2 as a carbonyl source, copolymerization of cyclic ethers and CO_2 have been intensively investigated (Fig. 1) (selected reviews[48–51] and selected recent papers[52–64]). Epoxides and oxetanes have been used as starting materials; however the copolymerization of CO_2 and cyclic ethers with five-membered or larger ring has not been reported at all because such cyclic ethers are difficult to be prepared due to the low stability. On the other hand, the direct polymerization of diols and CO_2 by dehydration condensation will enable the synthesis of polycarbonates containing longer alkyl chains (Fig. 1, this work). However, the dehydration condensation of diols and CO_2 is seriously limited by the reaction equilibrium. For example, it is well-known that the equilibrium yield of propylene carbonate from 1,2-propanediol and CO_2 on 1,2-propanediol basis has been estimated to be below 2%[65]. Regarding the direct synthesis of polycarbonates from α,ω-diols and CO_2, to the best of our knowledge, there are no reports on catalytic and non-catalytic synthesis methods, although conversion of CO_2, diols and dihalides to polycarbonates using K_2CO_3 was reported[66].

Herein, we demonstrate that the combination of CeO_2 catalyst and 2-cyanopyridine promoter is effective for the direct copolymerization of diols and CO_2. This is a first report on the catalytic direct synthesis of cooligomers from CO_2 and diols.

Results

Catalyst screening. First, the polymerization from CO_2 and 1,4-butanediol was investigated using various metal oxides with 2-cyanopyridine (Table 1). 2-Cyanopyridine was selected as a dehydrating agent because 2-cyanopyridine is preferable for the hydration over CeO_2[33–35,67,68]. The reaction was carried out with an autoclave reactor containing a metal oxide (0.17 g), 1,4-butanediol (10 mmol), 2-cyanopyridine (100 mmol) and CO_2 (5.0 MPa) at 403 K. Conversion and selectivity were calculated on the 1,4-butanediol basis. The detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S1. No oligomer product was obtained without a metal oxide catalyst (Table 1, entry 13). CeO_2 provided the oligomer in 97% yield (M_n = 1070, dispersity

Entry	Metal oxide catalyst	Conversion (%)	Selectivity (%)			M_n†	Dispersity‡
			Oligomer	4-Hydroxybutyl picolinate	Others		
1	CeO_2	>99	97	3	<1	1070	1.33
2	CeO_2§	99	98	2	<1	1150	1.31
3	La_2O_3	46	<1	23	77	–	–
4	ZnO	29	<1	2	98	–	–
5	TiO_2	24	<1	<1	>99	–	–
6	γ-Al_2O_3	22	<1	2	98	–	–
7	Nb_2O_5	13	<1	4	96	–	–
8	ZrO_2	3	<1	<1	>99	–	–
9	MgO	<1	–	–	–	–	–
10	SiO_2	<1	–	–	–	–	–
11	Pr_6O_{11}	<1	–	–	–	–	–
12	Y_2O_3	<1	–	–	–	–	–
13	none	<1	–	–	–	–	–

Table 1. Direct copolymerization of 1,4-butanediol and CO_2 using a metal oxide catalyst and 2-cyanopyridine[*]. [*]Reaction conditions: metal oxide 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 100 mmol, CO_2 5 MPa (at r.t.), 403 K, 8 h. †Based on crude sample, polystyrene equivalent molar mass (M_n(SEC)). ‡Dispersity is an index (M_w/M_n) determined by SEC with THF as eluent. §Second use.
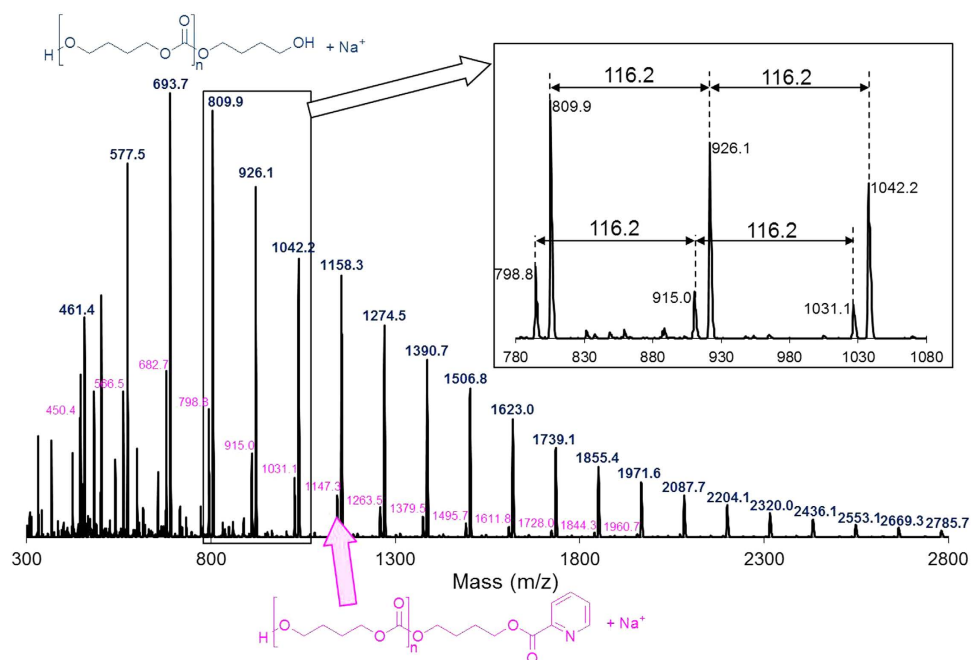

Figure 2. MALDI-TOF mass spectrum of the products from CO_2 and 1,4-butanediol using CeO_2 and 2-cyanopyridine.

(M_w/M_n) = 1.33) with slight amount of 4-hydroxybutyl picolinate, which was produced by 2-cyanopyridine and 1,4-butanediol (Table 1, entry 1), and the M_n of the oligomer corresponds to the oligomers formed from eight CO_2 and eight 1,4-butanediol. MALDI-TOF mass spectroscopy revealed the formation of the alternating cooligomer from CO_2 and 1,4-butanediol (Fig. 2), and confirmed no formation of the ether bond. In addition, 2-picolinamide was produced selectively by reaction of 2-cyanopyridine with H_2O that is produced by the copolymerization from CO_2 and 1,4-butanediol (Supplementary Table S1). On the other hand, other metal oxides showed lower conversion than CeO_2 and gave no oligomers (Table 1, entries 3–12). Others would include dimer, trimer or diester produced from 2-cyanopyridine and 1,4-butanediol. Therefore, among the metal oxides tested, CeO_2 is the only active metal oxide for the reaction by using 2-cyanopyridine as a dehydrating agent. It should be noted that CeO_2

Entry	2-Cyanopyridine [mmol]	Conv. [%]	Selectivity (%)			M_n[†]	Dispersity[‡]
			Oligomer	4-Hydroxybutyl picolinate	Others		
1	5	68	99	1	<1	510	1.14
2	10	93	98	2	<1	910	1.37
3	20	98	98	2	<1	1110	1.34
4	50	99	98	2	<1	1030	1.32
5	100	99	97	4	<1	1070	1.33
6	200	99	97	3	<1	900	1.33

Table 2. Effect of 2-cyanopyridine amount on the polymerization of 1,4-butanediol and CO_2 using CeO_2 catalyst[*]. [*]Conditions: CeO_2 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 5–200 mmol, CO_2 5 MPa (at r.t.), 403 K, 8 h. [†]Based on crude sample, polystyrene equivalent molar mass (M_n(SEC)). [‡]Dispersity is an index (M_w/M_n) determined by SEC with THF as eluent.

Entry	CO_2 pressure	Conversion (%)	Selectivity (%)			M_n[†]	Dispersity[‡]
			Oligomer	4-Hydroxybutyl picolinate	Others		
1	0.5	88	99	1	<1	630	1.24
2	1	93	99	1	<1	700	1.29
3	2	96	99	1	<1	790	1.31
4	3	98	99	1	<1	900	1.32
5	5	99	97	3	<1	1070	1.33

Table 3. Effect of CO_2 pressure on the polymerization of 1,4-butanediol and CO_2 using CeO_2 catalyst and 2-cyanopyridine[*]. [*]Reaction conditions: CeO_2 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 100 mmol, CO_2 0.5–5 MPa (at r.t.), 403 K, 8 h. [†]Based on crude sample, polystyrene equivalent molar mass (M_n(SEC)). [‡]Dispersity = polydispersity index (M_w/M_n) determined by SEC with THF as eluent.

alone without 2-cyanopyridine provided no oligomer (not shown). Taking this result into consideration, the combination of CeO_2 and 2-cyanopyridine is essential for the formation of the oligomer of 1,4-butanediol and CO_2. We first demonstrated direct copolymerization from CO_2 and 1,4-butanediol using the combination of CeO_2 catalyst and 2-cyanopyridine promoter. In addition, the reusability of CeO_2 catalyst was investigated. CeO_2 was easily retrieved from the reaction mixture by decantation, and the collected catalyst was washed with methanol, followed by calcining at 873 K for 3 h, and then the recovered CeO_2 was used for the next reaction. CeO_2 could be reused without remarkable loss of activity and selectivity (Table 1, entry 2), and XRD and BET analyses confirmed that the structure of CeO_2 was unchanged during the reusability test (Supplementary Fig. S1). In addition, the dissolved amount of Ce species in the filtrate was below the detection level (<0.1 %) of ICP-AES, which indicates that CeO_2 worked as a truly heterogeneous catalyst in this reaction.

Performance of combination of CeO_2 catalyst and 2-cyanopyridine promoter.
2-Cyanopyridine reacts with one mole of H_2O to provide 2-picolinamide, indicating that 10 mmol of 2-cyanopyridine is theoretically necessary to convert all of 1,4-butanediol to the corresponding oligomer when 10 mmol of 1,4-butanediol is used. Effect of 2-cyanopyridine amount was studied using CeO_2 catalyst (Table 2, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S2). 10 mmol and larger than 10 mmol of 2-cyanopyridine provided almost the same conversion and M_n (Table 2, entries 2–6), although 5 mmol of 2-cyanopyridine is not effective due to the smaller amount of 2-cyanopyridine than the theoretical amount (Table 2, entry 1). Therefore, the equivalent amount of 2-cyanopyridine is enough for the formation of the oligomer from 1,4-butanediol and CO_2.

Low CO_2 pressure is preferable from the environmental and economic viewpoints. The effect of CO_2 pressure was investigated using CeO_2 catalyst and 2-cyanopyridine promoter (Table 3, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S3). The reaction proceeds even at low CO_2 pressure of 0.5 MPa to give the oligomer in good yield (Table 3, entry 1), although the conversion and M_n gradually decreased with decreasing CO_2 pressure. This result provides the possibility to perform the reaction at low CO_2 pressure.

The time-course of the copolymerization of CO_2 and 1,4-butanediol was investigated using CeO_2 catalyst and 2-cyanopyridine promoter (Fig. 3, the detailed data are shown in Supplementary Table S4 and Supplementary Figs S2 and S3). The reaction rapidly proceeded to reach 99% conversion in one hour, and the high selectivity to the oligomer (≥97%) was maintained from the short reaction time, which strongly indicates that the oligomers were not produced via formation of tetramethylene carbonate, the corresponding cyclic carbonate. On the other hand, the M_n increased with the reaction time up to 8 h, but decreased gradually at more than 8 h. Dispersity also increased to about 1.3 in one hour and gradually increased at more than 1 h. The decrease of M_n and increase of dispersity are attributed to degradation of the oligomers and/or intramolecular termination by the nucleophilic attack of the OH group at the end of polymer, which is known as back-biting[69,70].
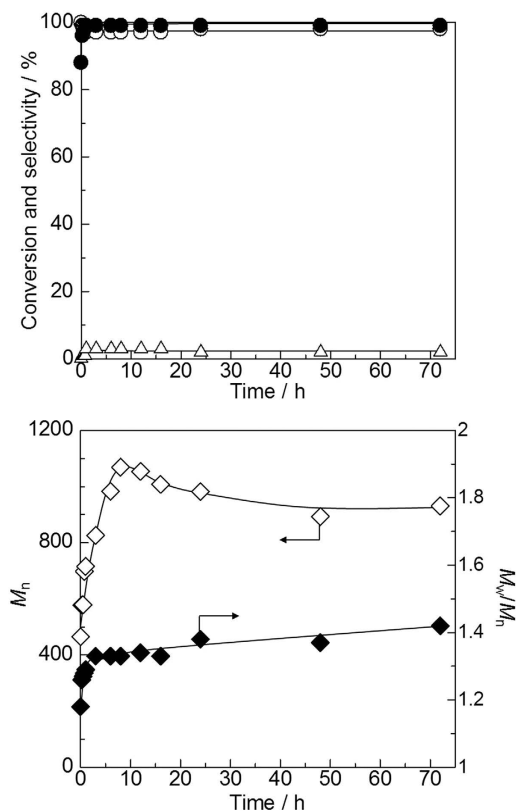
Figure 3. **Time-course of direct polymerization of 1,4-butanediol and CO_2 using CeO_2 catalyst and 2-cyanopyridine.** (**a**) Conversion and selectivity (●: conversion, ○: selectivity to oligomer, △: selectivity to 4-hydroxybutyl picolinate. (**b**) M_n and M_w/M_n (◇: M_n, ◆: M_w/M_n). Reaction Conditions: CeO_2 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 100 mmol, CO_2 5 MPa (at r.t.), 403 K.

| Diol | Conversion (%) | Selectivity (%) | | | M_n[‡] | Dispersity[§] |
		Oligomer	Ester[†]	Others		
1,4-Butanediol	>99	97	3	<1	980	1.38
1,5-Pentanediol	99	99	1	<1	930	1.34
1,6-Hexanediol	99	99	1	<1	1080	1.31
1,8-Octanediol	99	99	1	<1	1200	1.33
1,10-Decanediol	94	97	3	<1	1650	1.26
1,4-Cyclohexanedimethanol	41	98	2	<1	510	1.04
1,4-Benzenedimethanol	56	82	11	7	590	1.10
1,5-Hexanediol	93	99	1	<1	530	1.10
2,5-Hexanediol	6	60	2	38	450	1.01
2,5-Dimethyl-2,5-hexanediol	<1	–	–	–	–	–

Table 4. **Scope of diols in the direct polymerization of diol and CO_2 using CeO_2 catalyst and 2-cyanopyridine**[*]. [*]Conditions: CeO_2 0.17 g, diol 10 mmol, 2-cyanopyridine 100 mmol, CO_2 5 MPa (at r.t.), 403 K, 24 h. [†]Ester is formed from 2-cyanopyridine and diol. [‡]Based on crude sample, polystyrene equivalent molar mass (M_n(SEC)). [§]Dispersity is an index (M_w/M_n) determined by SEC with THF as eluent.

Finally, the scope of diols was investigated in the copolymerization of CO_2 and diols using CeO_2 catalyst and 2-cyanopyridine promoter (Table 4, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S5). Linear C4–C10 α,ω-diols were converted to the corresponding cooligomers in good yields. The corresponding cyclic carbonates were not also observed in the case of C5–C10 diols, which supports that the direct dehydration condensation of diols and CO_2 takes place in this reaction system. The average number of the repeating unit of these copolymers was 7 ~ 8 even with any diols. 1,4-Cyclohexanedimethanol and 1,4-benzenedimethanol, which are diols with rigid structure, were converted to the corresponding copolymers, however, the reactivity and M_n were lower than those of linear alkyl diols. To examine the effect of the position of the OH group, the combination of CeO_2 catalyst and 2-cyanopyridine promoter was applied to 1,5-hexanediol
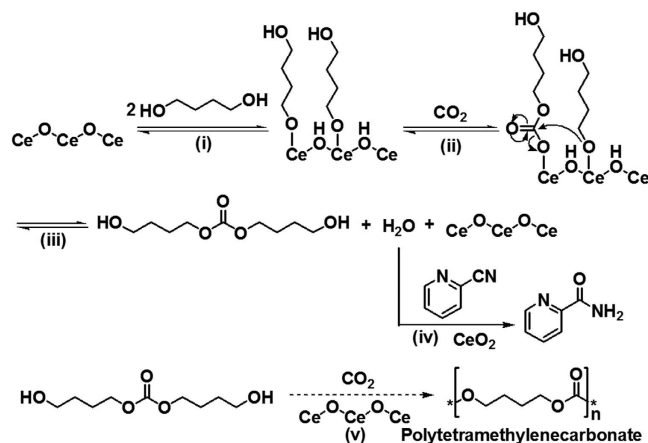
Figure 4. Proposed reaction mechanism of the formation of cooligomers from 1,4-butanediol and CO_2 using CeO_2 catalyst and 2-cyanopyridine.

having one primary and one secondary OH groups, 2,5-hexanediol having two secondary OH groups, and 2,5-dimethyl-2,5-hexanediol having two tertiary OH groups. 1,5-Hexanediol showed lower conversion, selectivity and M_n than 1,6-hexanediol having two primary OH groups. 2,5-Hexanediol showed further lower conversion, selectivity and M_n than 1,5-hexanediol. In the case of 2,5-dimethyl-2,5-hexanediol, the corresponding oligomer was not obtained. Therefore, steric hindrance around the OH group drastically decreases the substrate reactivity.

Proposed reaction mechanism. The proposed reaction mechanism is shown in Fig. 4. Based on the previous reports on carbonate synthesis from alcohol and CO_2 over CeO_2 catalyst[35], the reaction starts with (i) adsorption of diol on CeO_2 surface to form alkoxide adspecies. (ii) CO_2 insertion to the some alkoxide adspecies, providing some carbonate adspecies. (iii) Nucleophilic attack of the oxygen anion in the alkoxide adspecies to the carbonate adspecies to afford the corresponding carbonate from 1,4-butanediol and H_2O. (iv) Removal of the produced H_2O by hydration of 2-cyanopyridine to 2-picolinamide over CeO_2[33–35,67]. (v) Finally, further reaction of the produced carbonate with CO_2 1,4-butanediol or produced cooligomer, giving polytetramethylenecarbonate. Among these reaction steps, the step (iv) is very important in the polycarbonate synthesis, which will drastically shift the reaction to the product side by removal of H_2O from the reaction media.

Discussion

In summary, we first demonstrated the direct copolymerization from CO_2 and diols using the combination of CeO_2 catalyst and 2-cyanopyridine promoter. Various diols including α,ω-diols with long alkyl chain can be transformed to the corresponding cooligomers, which cannot be obtained by the conventional methods with cyclic carbonate, epoxides or oxetanes. This catalyst system will not only open up a new epoch for polymer chemistry, particularly polycarbonate synthesis, but also make a large impact on transformation of CO_2.

Methods

Materials. Preparation of CeO_2 catalyst was carried out by calcining CeO_2-HS (Daiichi Kigenso, Japan. The purity of CeO_2: 99.97%) for 3 h in air at 873 K. The specific surface area (BET method) of the CeO_2 was 84 m^2/g. All the chemicals for organic reactions were commercially available and were used without further purification. Other metal oxides were commercially available or synthesized by the precipitation method: ZrO_2 (Daiichi Kigenso Kogyo Co. Ltd., $Zr(OH)_4$ was calcined under air at 873 K for 3 h.), MgO (Ube Industries, Ltd., MgO 500A, 873 K, 3 h), TiO_2 (Nippon Aerosil Co. Ltd., P-25), γ-Al_2O_3 (Nippon Aerosil), ZnO (FINEX-50, Sakai Chemical Industry Co.,Ltd), SiO_2 (Fuji Silysia Chemical Ltd., 773 K, 1 h), Nb_2O_5 (Companhia Brasileira de Metalurgia e Mineracao (CBMM), $Nb_2O_5 \cdot nH_2O$ was calcined at 773 K for 3 h). Y_2O_3, La_2O_3 and Pr_6O_{11} were prepared by the precipitation method. $Y(NO_3)_3 \cdot nH_2O$ (Wako Pure Chemical Industries Ltd., >99.9%), $La(NO_3)_3 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd., >99.9%) and $Pr(NO_3)_3 \cdot nH_2O$ (Wako Pure Chemical Industries Ltd., >99.5%) were used as precursors. A precursor (25 g) was dissolved in water (100 ml) and NH_3aq (1 M) was dropped with stirring until the pH of the solution became 10, resulting in a precipitate. The precipitate was filtered and washed by water, followed by drying at 383 K overnight (12 h) and calcining under air at 873 K (673 K for La_2O_3) for 3 h.

Typical procedure for direct polymerization of CO_2 and 1,4-butanediol. All the reactions were carried out in an autoclave reactor with an inner volume of 190 mL. The standard procedure of direct polymerization of CO_2 and 1,4-butanediol using the combination catalyst of CeO_2 and 2-cyanopyridine was as follows: CeO_2 (0.17 g, 1 mmol), 1,4-butanediol 0.90 g (10 mmol) and 2-cyanopyridine 10.4 g (100 mmol) were put into the autoclave together with a spinner, and then the reactor was purged with 1 MPa CO_2 (Shimakyu Co. Ltd., >99.5%) three times. The autoclave was pressurized with CO_2 to the desired pressure (typically 5.0 MPa) at room

temperature, and then the autoclave was heated to 433 K, where the CO_2 pressure was about 12 MPa. The mixture was constantly stirred during the reaction. After the reaction time, the reactor was cooled in water bath to room temperature. THF (20 ml) was added to the liquid phase as a solvent, and 1-hexanol (~0.2 ml) was also added as an internal standard substance for a quantitative analysis. The reactor was washed with THF, and the liquids used in washing were added to the reaction mixture. Amount of 2-cyanopyridine and products from 2-cyanopyridine such as 2-picolinamide and 4-hydroxybutyl picolinate were analyzed by gas chromatography (Shimadzu GC-2014) equipped with an FID using a CP/Sil 5 CB. Since produced cooligomers is decomposed by heating, the amount of 1,4-butanediol was analyzed by HPLC (Shimazu Prominence) equipped with an RI detector (RID-10A) using a Pheny-Hexyl Luna column (Phenomenex, particle size 5 μm, 250 mm × 4.6 mm, conditions: developing solvent, H_2O/CH_3OH = 70/30, 0.5 ml/min, 313 K). Since produced cooligomers were precipitated by addition of the developing solvent (about 20-fold dilution), the precipitated cooligomers were removed by filtration before analyzing by HPLC. This filtration operation was conducted at least two times until the precipitation was not observed. The qualitative analysis of the products were conducted by a gas chromatograph equipped with a quadrupole mass spectrometer (GC-MS, Shimazu QP5050) using the same capillary columns and NMR (Bruker, AV400). The oligomerized products were analyzed by MALDI-TOF mass (Shimazu AXIMA-CFR Plus) using dithranol and NaBr as a matrix and ionization agent, respectively, and size exclusion chromatography (SEC, Shimazu Prominence) with a RI detector (RID-10A) using a Shodex HPLC column KF-805L. The developing solvent is THF (Wako Pure Chemical Industries, >99.5%).

The conversion and selectivity were calculated by the following equations (Eqs 1–3).

$$\text{Conversion/\%} = 100 \times [1 - (\text{Amount of diol after reaction (mmol)}) / (\text{Amount of diol before the reaction (mmol)})] \qquad (1)$$

$$\text{Selectivity/\%} = 100 \times [(\text{Amount of the product (mmol)}) \times (\text{number of diol units in the product}) / (\text{amount of reacted diol (mmol)})] \qquad (2)$$

$$\text{Yield/\%} = \text{Conversion(\%)} \times \text{selectivity(\%)}/100 \qquad (3)$$

The amount of oligomer was determined by subtraction of the amount of the produced ester from the amount of reacted diol. The products in which the signal was not observed by SEC were assigned to others.

Catalyst characterization.

The surface area of CeO_2 was measured with BET method (N_2 adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded using MiniFlex 600 with Cu $K\alpha$ (40 kV, 15 mA) radiation. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500).

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Author Contributions

M.T. and K.T. conceived the concept and directed the project. I.K., M.T. and H.M. conducted experiments. M.T., Y.N. and H.S. discussed the experiments and results, and prepared the manuscript.

Additional Information

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