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Supporting Information

for

Efficient Low-Temperature Depolymerization of Polycarbonate

Catalyzed by Lanthanum β-Diketonate Complexes

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SI-1 General Information

NMR spectra were recorded on a ECZ-500R spectrometer, operating at 500 MHz for ¹H, 125 MHz for ¹³C NMR in CDCl₃. CDCl₃ (δ = 7.26 ppm) was used as the internal standard for ¹H NMR, CDCl₃ (δ = 77.0 ppm) was used as the internal standard for ¹³C NMR.

GC spectra were recorded on a Shimadzu GC-2030AF, 100V spectrometer using SH-Rtx-5 Amine column (30 m, 0.25 mmID, 0.25 μ m df) with following conditions: gas pressure: 274.1 kPa; total flow: 204.4 mL/min; column flow: 6.35 mL/min; velocity: 87.1 cm/sec; purge flow: 3.0 mL/min; sprit ratio: 30.7; injector: 280 °C, FID: 320 °C; column program: starting from 40.0 °C for 5 min, then 10 °C/min to 110 °C, then 15 °C/min to 290 °C, 10 min hold. Electrospray Ionization time of flight mass spectrometry (ESI-TOF-MS) analyses were performed on Bruker Compact System.

Infrared (IR) spectra were obtained using a Shimadzu IR Spirit spectrometer. Data are expressed as the transmittance relative to wavenumbers.

The molecular weight distribution curves, number-average molecular weight (Mn), peak molecular weight (Mp) and dispersity (Mw/Mn) of the polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 40 °C (flow rate: 1.0 mL min⁻¹) equipped with linear-type polystyrene gel columns (KF-G 4A;particle size=8 μ m, 4.6 mm i.d. × 100 mm, KF-805L;exclusion limit=4 × 10⁶ mol g⁻¹, particle size=10 μ m, pore size=5000 Å, 8.0 mm i.d. × 300 mm, Shodex, Tokyo, Japan) connected to a SPD-10A Ultraviolet (UV) detector set at 245 nm (Shimadzu corporation, Kyoto, Japan). The columns were calibrated against 12 standard Polystyrene (PS) sample (TOSOH, Tokyo, Japan; Mn=450–1110000 g mol⁻¹, Mw/Mn=1.08–1.16).

The organic solvents used in this study, including methanol, were commercially available. They were properly distilled under an argon atmosphere and stored in a molecular sieve 4A before use.

Poly(Bisphenol A) carobonate (PC) for a standard sample of this study was purchased from Thermo Fisher Scientific Inc. as a granular form.

SI-2 Experimental Procedures

Preparation of ligands

The ligands were used as received from commercial suppliers without further purification, except for the following ligands (2b, 2f, 3a–h, 4c).

Synthesis of 2,6-dimethyl-3,5-heptadione (2b)¹ *t*-BuOK (16.8 g, 150 mmol, 1.5 eq.) was suspended in 30 mL of dry DMF and heated to 50 °C in an oil bath. The mixture of 3-methyl-2-butanone (8.6 g, 100 mmol, 1 eq.) and ethyl 2-methylpropanoate (34.6 g, 300 mmol, 3 eq.) was added dropwise over 60 min. The mixture was stirred for 16 hours at that temperature. After cooling to room temperature, the solution was diluted with 300 mL of 2.5 M HCl and the pH of aqueous phase was adjusted to 1-2. The aqueous phase was extracted with a mixture of ethyl acetate/*n*-hexane = 1/4 (3 x 20 mL). Combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and filtrated. After removing of solvents by evaporation, the crude mixture was purified by distillation (85 °C, 2.6 kPa) to give 2,6- dimethyl-3,5-heptadione as a yellowish oil in 73 % yield (11.3 g, 72.6 mmol).

¹H NMR (500 MHz, CDCl₃); (diketone tautomer, only small traces of enol tautomer are present in the spectrum) δ 5.46 (s, 2H), 2.47-2.38 (m, 2H), 1.09 (d, 12H): ¹³C NMR (125 MHz, CDCl₃); δ 199.1, 95.0, 36.8, 19.4 ppm.

ESI-MS: calcd for C₉H₁₇O₂ [M+H]+: 157.12; found 157.12.

Synthesis of the 1,3-Bis(pyridin-2-yl)propane-1,3-dione (2g)² 2-Acetylpyridine (1.83 g, 15.0 mmol) was dissolved in 40 mL of dry THF. *t*-BuOK (2.52 g, 22.5 mmol, 1.5 eq.) was carefully added to the solution at 0 °C. To this mixture was then added ethyl picolinate (6.81 g, 45.0 mmol, 3.0 eq.), and the mixture was vigorously stirred at 60 °C for 16 h. The solvent was eventually removed by evaporation and the resulting solid was added to a mixture of glacial acetic acid / water = 1/5. The remaining solid was filtered and washed with water, small amount of methanol. The crude mixture was purified on a silica gel column chromatography (n-hexane/ ethyl acetate/CHCl₃ = 2/1/1) to give **2f** (2.15 g, 9.49 mmol, 63 % yield).

¹H NMR (500 MHz, CDCl₃); (enol:keto=87:13) enol, δ 8.63 (dd, 2H), 8.04 (dd, 2H), 7.76-7.72 (ddd, 2H), 7.33-7.31 (ddd, 2H); keto, δ 8.48 (dd, 2H), 7.98 (dd, 2H), 7.71 (m, 2H), 7.34 (m, 2H): ¹³C NMR (125 MHz, CDCl₃); δ 197.0, 184.4, 152.6, 152.3, 149.4, 148.9, 137.0, 136.9, 127.3, 126.5, 122.1, 121.9, 94.6, 48.3 ppm.

ESI-MS: calcd for C₁₃H₁₁N₂O₂ [M+H]+: 227.08; found 227.08.

Synthesis of Acetylmesitylene³

Mesitylene 7.81 mL (6.61 g, 55 mmol, 2 eq.) and $Sc(OTf)_3$ 0.44 g (0.9 mmol, 3.3 mol%) were placed in three-necked flask and then stirred in ice-bath under Ar atmosphere. TFAA 5.72 mL (8.63 g, 41 mmol, 1.5 eq.) was added dropwise with stirring, and the mixture was stirred at 0 °C for 30 min. Acetic acid (1.64 g, 27 mmol, 1 eq.) was added slowly, and the reaction was continued for 3 h at 30 °C. The mixture was then poured into 100 mL of water, and the organic phase was separated. The aqueous phase was extracted with

a mixture of diethyl ether/n-hexane = 1/20 (3 x 20 mL), and the combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and filtrated. After removing of the solvent by evaporation, the resulting crude mixture was purified by silica gel column chromatography (diethyl ether/n-hexane = 1/20) to give acetylmesitylene as pale yellow solid in 99 % yield (4.40 g, 27 mmol).

¹H NMR (500 MHz, CDCl₃); δ 6.84 (s, 2H), 2.46 (s, 3H), 2.28 (s, 3H), 2.22 (s, 6H).

General procedure for the synthesis of 1-aryl-1,3-but adione (3a-h) and ethyl (3,4-dimethoxybenzoyl)acetate $(4c)^4$

To a suspension of NaH (1.60 g of dispersion in oil, 40 mmol, 4 eq.) in EtOAc (20 mL) or diethyl malonate (20 mL, for the case of **4c**) was slowly added a solution of 1-arylethanone (10 mmol) in EtOAc (20 mL) or diethyl malonate (20 mL, for the case of **4c**) at 0 °C, and the resulting mixture was stirred at room temperature overnight. Then the mixture was carefully poured into 10% aq. NH₄Cl (30 mL) and the pH was adjusted to be 5 with HCl. The aqueous phase was separated and extracted with EtOAc. The combined organic phase was dried over Na₂SO₄, and after removing the solvent by evaporation, the resulting crude mixture was purified by silica gel flash column chromatography (n-hexane /EtOAc = 10:1) to give 1-aryl-1,3-butadione (**3a-h**) or ethyl (3,4-dimethylbenzoyl)acetate (**4c**) (keto-enol mixture).

1-(4-Methylphenyl)-1,3-butanedione (3a)

55 % yield

¹H NMR (500 MHz, CDCl₃); δ 7.78 (d, 2H), 7.30 (dd, 2H), 6.16 (s, 1H), 2.39 (s, 3H), 2.17 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 193.1, 183.8, 143.1, 132.2, 129.4, 127.1, 96.4, 25.6, 21.6. ESI-MS: calcd for C₁₀H₁₂NaO₂ [M+Na]+: 199.07; found 199.07.

1-(2,4,6-Trimethylphenyl)-1,3-butanedione (3b)

79 % yield ¹H NMR (500 MHz, CDCl₃); δ 6.89 (s, 2H), 5.64 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.18 (s, 3H) : ¹³C NMR (125 MHz, CDCl₃); δ 194.5, 187.9, 138.9, 134.8, 134.2, 128.5, 103.1, 26.1, 21.2, 19.7. ESI-MS: calcd for C₁₃H₁₆NaO₂ [M+Na]+: 227.10; found 227.11.

1-(4-Fluorophenyl)-1,3-butanedione (3c)

95 % yield ¹H NMR (500 MHz, CDCl₃); δ 7.84-7.87 (m, 2H), 7.06-7.10 (m, 2H), 6.10 (s, 1H), 2.15 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 192.9, 183.0, 165.4 (d, *J*=252 Hz), 131.3 (d, *J*=3 Hz), 129.5 (d, *J*=9 Hz), 115.8 (d, *J*=22 Hz), 96.4, 25.5.

ESI-MS: calcd for C₁₀H₉FNaO₂ [M+Na]+: 203.05; found 203.05.

1-(4-Trifluoromethylphenyl)-1,3-butanedione (3d)

50 % yield

¹H NMR (500 MHz, CDCl₃); δ 7.97 (d, 2H), 7.70 (d, 2H), 6.20 (s, 1H), 2.24 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 195.2, 181.0, 138.2, 133.6 (q, *J*=32.6 Hz), 127.4, 125.7 (q, *J*=3.6 Hz), 123.8 (q, *J*=270.9 Hz), 97.4, 26.2.

ESI-MS: calcd for $C_{11}H_{10}F_3O_2$ [M+H]+: 231.06; found 231.06.

1-(4-Methoxylphenyl)-1,3-butanedione (3e)

89 % yield

¹H NMR (500 MHz, CDCl₃); δ 7.66-7.69 (m, 2H), 6.73-6.75 (m, 2H), 5.95 (s, 1H), 3.64 (s, 3H), 1.99 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 191.6, 184.1, 163.1, 130.9, 129.1, 113.9, 95.7, 55.2, 25.0. ESI-MS: calcd for C₁₁H₁₃O₃ [M+H]+: 193.09; found 193.09.

1-(3,4-Dimethoxyphenyl)-1,3-butanedione (3f)

97 % yield

¹H NMR (500 MHz, CDCl₃); δ 7.42-7.44 (dd, 1H), 7.40 (d, 1H), 6.83 (d, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.11 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 190.7, 184.8, 152.8, 149.0, 128.0, 121.2, 110.5, 109.6, 95.9, 56.2, 56.1, 25.0.

ESI-MS: calcd for C₁₂H₁₅O₄ [M+H]+: 223.10; found 223.10.

1-(2,4,6-Trimethoxyphenyl)-1,3-butanedione (3g)

72 % yield ¹H NMR (500 MHz, CDCl₃); δ 6.11 (s, 2H), 5.71 (s, 1H), 3.79 (s, 9H), 2.10 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 189.5, 186.2, 162.7, 159.0, 112.3, 104.4, 90.8, 56.0, 55.5, 24.8. ESI-MS: calcd for C₁₃H₁₇O₅ [M+H]+: 253.11; found 253.11.

1-(3,4,5-Trimethoxyphenyl)-1,3-butanedione (3h)

93 % yield ¹H NMR (500 MHz, CDCl₃); δ 7.12 (s, 2H), 6.11 (s, 1H), 3.92 (s, 6H), 3.92 (s, 3H), 2.16 (s, 3H): ¹³C NMR (125 MHz, CDCl₃); δ 191.6, 184.1, 153.2, 141.8, 130.3, 104.4, 96.3, 60.9, 56.2, 25.3. ESI-MS: calcd for C₁₃H₁₇O₅ [M+H]+: 253.11; found 253.11.

Ethyl (3,4-dimethoxybenzoyl)acetate (4c)

83 % yield

¹H NMR (500 MHz, CDCl₃); δ 7.46-7.49 (m, 2H), 6.83-6.84 (d, 1H), 4.12-4.16 (q, 2H), 3.86-3.89 (m, 7H), 1.18-1.21 (t, 3H): ¹³C NMR (125 MHz, CDCl₃): δ 191.1, 167.8, 153.9, 149.2, 129.3, 123.6, 110.3, 110.1, 61.4, 56.1, 56.0, 45.7, 14.1.

ESI-MS: calcd for C₁₃H₁₇O₅ [M+H]+: 253.11; found 253.11.



Figure S1. Structure of synthesized lignads.

General procedure for preparation of PC powder

PC (20.1 g) in pellet form was added to toluene (2 L) and stirred at room temperature for more than 12 h. The obtained white suspension was filtered through a stainless steel mesh with an aperture of 500 μ m. The solvent was then removed under reduced pressure to obtain a white solid. The white solid was ground in a mortar and dried under vacuum at 80 ° C overnight to obtain a white powder (6.6 g). Particle size distribution measurement in methanol confirmed that the prepared PC powder possessed two peaks of 105 μ m and 384 μ m.

General procedure for methanolysis of PC powder

PC powder (101.7 mg, 0.4 mmol, based on the BPA-CO unit) and a La complex (4 μ mol, 1 mol% relative to PC) were placed in a sealed tube reactor. Methanol (4 mL) was added to the reactor, and the atmosphere was replaced with argon. The reactor was then sealed tightly and stirred at 60 ° C for 2 h. After this period, the reactor was allowed to cool to room temperature. Decane was added as an internal standard, and the mixture was diluted with methanol. After removing the reaction residue with a membrane filter, the methanol solution was analyzed by GC-FID.

Polymerization reaction with bisphenol A and diphenylcarbonate

Polymerization to give PC was followed by a described procedure^{5,6}. Bisphenol A (BPA) 1.15 g (5.04 mmol, TCI, Japan) and diphenyl carbonate (DPC) 1.19 g (5.56 mmol, 1.1 equiv., TCI, Japan) were placed in a 300 mL autoclave in the air. LiOH H₂O 75.8 mg (1.81 mmol, FUJIFILM Wako Pure Chemical Corp.) as supplied was diluted with deionized water in 2 L volumetric flask, and used as stock solution. Then 5 mL of the stock solution was added into autoclave reactor. The reactor was sealed and stirred in oil bath at 230 °C for 4h. After the reaction was completed, the reactor was cooled to room temperature and a precipitate

formed was dissolved in chloroform. After removing solvent, the resulting reaction mixture was dried in vacuo and analyzed by GPC.

Then the mixture was dissolved in small amount of THF (5 mL), and dropwisely added onto methanol (500 mL) with stirring. The precipitate generated was collected by filtration, the solution was evaporated, and the precipitate was dried in vacuo. The precipitate and the residue were analyzed by GPC.



Scheme S1. Polymerization of Bisphenol A and diphenylcarbonate.



Figure S2. GPC chromatogram of synthesized PC sample (Reaction mixture). Flow rate: 1.0 mL/min, Eluent: THF, Column: KF-G 4A + KF-805L, Detect: UV (245 nm), Sample: ca. 0.2 wt%

SI-3 Particle Size Distribution Analysis

Particle size distribution of a powdered PC sample was analyzed by using a particle analyzer, Microtrac MT3300 (LOW-WET) (MicrotracBEL Corp.). After treatment using toluene, obtained PC solution was evaporated and dried in vacuo. The residue was ground with mortar. The resulting PC powder was subjected to measurement using methanol as a solvent after short sonication. Results of the distribution were shown in Figure S3. This measurement was performed by technical support of Mitsui Chemical Analysis & Consulting Service, Inc.

The powdered PC sample started with an apparent single broad peak, which split into a single peak and a single shoulder peak when sonicated, and converged with no variation after 15 minutes. The primary particle size at convergence was 105 µm and the secondary particle size was 384 µm. This flocculation mechanism is considered to be due to the classical interparticle bridging type by nonionic polymers⁷, and from the SEM images (SI-4) described below, the powder obtained by pretreatment in toluene is not an flocculation of two or more PCs with different solubility and molecular weight that further flocculates to form a single particle, It was determined that the primary particles formed by flocculation in toluene were further flocculated to form secondary particles.

Although toluene is not a solvent that completely dissolves PC, it can lower the interfacial free energy by adsorbing on the polymer surface, allowing spontaneous dispersion without external force. An adsorption layer was formed at the interface of the dispersed primary particles, and secondary particles were formed by the cohesive force between molecular chains in the adsorption layer, but this cohesive force is relatively weak and expected to be partially dispersed by ultrasonic^{8,9}.



Figure S3. Particle Size Distribution of powdered PC in methanol solution.

SI-4 SEM images

The surface morphology of the powdered PC was examined by a scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan). Result of the d surface images are shown in Figure S4. As shown in the results of the particle size distribution measurement, particles as small as 100 μ m can be observed in the image. Furthermore, these particles are an agglomeration of smaller particles (<1 μ m), forming a particle with a large surface area as a whole.



Figure S4. FE-SEM images of the powdered PC.

SI-5 GPC Analysis

Average molecular weight distribution analysis of the powdered PC sample was performed based on a calibration curve of polystyrene (PS). Monodisperse PS (TSKgel A-500, A-1000, A-2500, A-5000, F-1, F-2, F-4, F-10, F-20, F-40, F-80 and F-128, Tosoh Corporation) was used as reference samples, and the calibration curve was fitted as follows (Figure S5).



Figure S5. Chromatogram of GPC analysis and calibration curves for standard PS. Flow rate: 1.0 mL/min, Eluent: THF, Column: KF-G 4A + KF-805L, Detect: UV (245 nm), Sample: ca. 0.2 wt%

#	Retention time [min]	Molecular Weight	Frror [%]
11	Recention time [mm]	Wolceulai Weight	
1	6.45	1110000	-1.93
2	6.68	720000	-6.42
3	7.10	397000	6.18
4	7.47	225000	9.48
5	7.88	110000	5.87
6	8.43	37200	-11.80
7	8.87	17300	-13.47
8	9.28	8840	-8.81
9	9.62	5520	5.33
10	10.03	3120	21.73
11	10.41	1120	-3.55
12	10.70	589	-8.90

Table S1. Molecular weight of standard PS and Retention time under measurement conditions.

Results of GPC analysis data of PC pellet purchased from Thermo Fisher Scientific Inc. and powdered PC following the general procedure were as follows (Figure S6). This result indicates that there is no variation in molecular weight during the dispersion and milling with mortar processes in the powdering process. On the other hand, the average molecular weight is increased because highly soluble oligomeric components were removed by filtration.



Figure S6. Chromatogram of GPC analysis: (a)Pellet of PC, (b)Powdered PC. Flow rate: 1.0 mL/min, Eluent: THF, Column: KF-G 4A + KF-805L, Detect: UV (245 nm), Sample: ca. 0.2 wt%.

Table S2. Molecular weight of standard PS and Retention time under measurement conditions.

Detect: UV (245 nm)							
PC Sample	Mn	Mw	Mz	Mw/Mn			
Pellet of PC	18500	47000	75800	2.54			
Powdered PC	29100	49500	74100	1.70			

SI-6 Tracking of Molecular Weight Distribution

GPC analysis was performed at each reaction time to track changes in molecular weight during Methanolysis. PC powder or pellet ca.100 mg (0.4 mmol, as BOA-CO unit) and La-3f complex (4 μ mol, 1 mol%, 1:3 complex, as anhydride) were put into a sealed tube reactor, and to this mixture was added by methanol (4 mL) by added. After substituting Ar in the reactor, it was sealed tightly and stirred at 60 °C for each time. After the reaction, the reactor was allowed to cool to room temperature and removed methanol by evaporation. All residues were dissolved in THF and analyzed by GPC (Figure 4, Figure S7). GC analysis at 2 hours after heating showed that both BPA and DMC were not detected.



Figure S7. Time-resolved GPC analysis of methanolysis reaction with PC pellet.

SI-7 GC Analysis

To calculate the reaction yield by GC analysis, a calibration curve was prepared using decane as an internal standard. Retention times for BPA, DMC and decane under the same measurement conditions are shown in Figure S8. Unless otherwise noted, yields of BPA and DMC by methanolysis were calculated based on the calibration curves obtained (Figure S9).







Figure S9. Calibration curve for GC analysis using decane as internal standard.

SI-8 Isolation of Bisphenol A

PC powder (1.02 g, 4 mmol) and La complex with **3f** ligand(0.03 g, 0.04 mol, anhydride basis) were put into a 100 mL flask, and methanol (40 mL) was added. The mixture was stirred at 60 °C for 24 h. After the reaction, the flask was allowed to cool to room temperature. Then the solvent was removed by evaporation and the residue was purified by silica gel flash column chromatography using Et₂O as an eluent to give bisphenol A (0.91 g, 98.9 % yield) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 7.09 (d, 4H), 6.73 (d, 4H), 4.71 (s, 2H), 1.62 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 153.2, 143.3, 127.9, 114.7, 41.7, 31.0.

Dimethyl carbonate should be isolated by careful distillation of the solvent removed, but we have not conducted in this study.



Figure S10. ¹H and ¹³C NMR of isolated BPA.

SI-9 Reaction of Post-consumer PC Sample

As an example of implementation-oriented investigation on polycarbonate waste, we tried methanolysis of discarded safety goggles. In this study, a safety goggles purchased from UVEX, type X-9302, were used. After removing the transparent part of the goggles, it was cut into pieces of about 30 mm square to be placed in a flask and stirred in a large amount of toluene overnight. The obtained white suspension was filtered through a mesh made of SUS with an aperture of 500 μ m, then the solvent was removed and dried under reduced pressure to obtain a white solid. The white solid was ground in a mortar and dried under vacuum at 80 °C overnight to obtain bluish white powder.

The powder obtained and the sample made from PC pellets using the same procedure were compared using IR spectrum measurement: The two spectra showed good agreement and it was determined that the main component of the safety goggles was PC made of BPA.

The powder of safety goggles (101.7 mg, 0.4 mmol) and La complex (4 μ mol, 1 mol%; 1:3 complex, as anhydride) were put into a sealed tube reactor and methanol (4 mL) was added. After substituting Ar in the vessel, the vessel was heated to 60 °C with stirring. After 2 h, the vessel was allowed to cool to room temperature. Decane was added as an internal standard and the mixture was diluted with methanol. After removing the reaction residue with a membrane filter, the methanol solution was subjected to GC analysis.

GC analysis results showed that BPA and DMC were also being produced from the safety goggles. The yield was lower than that of the powder prepared from PC pellets, but this is because commercially available PC generally contains various additives such as stabilizers¹⁰. However, the yield of the monomer was greatly improved compared to the case of no catalyst and it was shown that the complex prepared in this study is useful for the chemical recycling of waste polycarbonate.

This finding indicates that the reaction progress is equivalent when using PC powder recycled from polycarbonate products and PC powder prepared from reagent-grade PC pellets. However, it should be noted that comparing our results using actual products with those of other studies performing similar experiments possess limitations due to the difficulty of conducting a rigorous characterization of the products involved. Our demonstration using plastic products aims to show that the reaction acceleration achieved by our pre-treatment process is not limited to virgin polycarbonate.



Figure S11. IR spectra of each PC samples.



safety goggles

Scheme S2. Methanolysis of post-consumer PC.

Enter	ntry PC sample	Catalwat / Ligand	Yield / %ª		
Entry		Catalyst / Ligaliu —	BPA	DMC	
1	1 1 11 /	None	N.D.	trace	
2	powdered pellet	La complex / 3f	70	68	
3	powdered safety	None	N.D.	trace	
4	goggles	La complex / 3f	59	61	

Table S3. Methanolysis of PC samples.

^a Determined by GC analysis using decane as internal standard.

SI-10 Additional Study for Recovery of Toluene and its Reuse

The details for recovery of toluene were explained as follows (Figure S12):

PC (3.0 g) in pellet form purchased from Thermo Fisher Scientific Inc., was added to toluene (500 mL) and stirred at room temperature for more than 12 h. Theis resulted in formation of white suspension (**Susp.** 1-1), and this was filtered through a stainless-steel mesh with an aperture of 500 μ m to separate remaining residue and a slurry (**Susp. 1-2**). The remaining residue, i.e., the relatively large PC particle, was dried to yield 0.4 g of white powder. According to the standard method shown in SI-2, this suspension is concentrated in an evaporator to obtain pc powder.

In the following additional experiments, we considered two methods for recovering toluene from the slurry (**Susp. 1-2**) that passed through the 500 μ m mesh. First, as in the general procedure, we used a rotary evaporator to separate toluene from the slurry and obtained a recovered toluene (**Recov. Tol A**). Then, 3.1 g of PC pellets were added to the obtained **Recov. Tol A** and stirred at room temperature for 12 hours, resulting in a white suspension (**Susp. 2-1**) similar to the first use. When this was filtered through a 500 μ m mesh, it was separated into the component that did not pass through the mesh (0.6 g after drying) and the slurry (**Susp. 2-2**). The recovered toluene (**Recov. Tol A**) did indicate to be used for the second dispersion.

On the other hand, since PC is not dissolved in the slurry (**Susp. 1-2**), it is possible to separate only the solids form liquid using a laboratory filter paper. When a separately prepared **Susp. 1-1** was filtered using a filter paper with a pore size of $<5 \mu$ m, it was possible to separate it into a white powder weighing 2.3 g after drying and a transparent recovered toluene (**Recov. Tol B**). This means that about 10% of the used PC (3 g) was converted into oligomers that dissolve in toluene by the dispersion process and remained in the recovered toluene. Alternatively, this residual part may have been a soluble component that was originally contained in the used PC as an impurity or additive. Separately, the white PC powder filtered from **Susp. 1-2** and the **Recov. Tol. B** were analyzed by GPC. We have confirmed that the recovered toluene layer contains PC oligomers with Mw of about 8400, and that the composite waveform with the filtered powder almost matches the molecular weight distribution of the pellets (Figure S13). Also, GC analysis of the **Recov. Tol B** confirmed that it did not contain BPA.

Next, the recovered toluene (**Recov. Tol B**) separated by filtration was also reused in the same way as the **Recov. Tol A**. That is, 3.0 g of PC pellets were added to **Recov. Tol B** and stirred at room temperature for 12 hours. In this case, also, a white suspension (**Susp. 3-1**) was obtained, as in the first use. When this was filtered through a 500 μ m mesh, it was possible to separate it into a component that did not pass through the mesh (1.3 g after drying) and a slurry (**Susp. 3-2**).

Finally, the obtained **Susp. 2-2** and **Susp. 3-2** were each filtered using filter paper, and the powder remaining on the filter paper was dried, resulting in 2.4 g of white powder from **Susp. 2-2** and 1.7 g of white powder from **Susp. 3-2**.



Figure S12. Additional experiments for recovery and reuse of toluene

These experiments conclude that **toluene can be recovered and reused**, and in more detail, they can be summarized as follows.

1) PC powder that can be adopted into methanolysis at 60 °C can be obtained from the suspension by evaporation or by filtration.

2) Similarly, the toluene used for dispersion can be recovered by separation using an evaporator or by filtration, and electric power consumption is not essential.

3) When recovering the toluene by filtration, care must be taken to avoid a decrease in dispersion efficiency due to components remaining in the solution.

Although this was not addressed in this study, there remains a good chance that filtration recovery may be able to remove residual material by using various adsorbents.



Figure S13. Chromatogram of GPC analysis: (A) Pellet of PC, (B) Dispersion PC (Powdered PC), (C) Dissolved in toluene, (D) (B)+(C). Flow rate: 1.0 mL/min, Eluent: THF, Column: KF-G 4A + KF-805L, Detect: UV (245 nm), Sample: ca. 0.2 wt%.

Table S4. Molecular weight of each PC sample. Average of molecular weight was obtained from the calibration curve in Figure S12.

		U		
PC Sample	Mn	Mw	Mz	Mw/Mn
Pellet of PC	13300	46800	75100	3.51
Powdered PC (Dispersion)	25500	58200	221200	2.28
Dissolved in toluene	2500	5400	8400	2.19

SI-11 Literature Survey on Methanolysis of PC and Comparison with This Study

In the methanolysis of PC, the use of a co-solvent is not only effective in lowering the temperature required for the reaction, but also can reduce usage of methanol which has been pointed out as being toxic; thus research is still continuing. On the other hand, THF, which is used in many papers as a co-solvent, is not necessarily ideal from a viewpoint of safety and toxicity. In addition, when attempting to reuse, it is also necessary to consider the extra effort required for separation from methanol.

From these aspects, research is also continuing on the use of methanol-sole system. If methanol is used as a sole solvent, the cost required for reusing it will be suppressed. On the other hand, as is clear from the table below, in the case of methanolysis using methanol as a sole solvent, it is a fact that many reactions are often carried out at higher temperatures than in co-solvent systems. There are no examples of reactions carried out below the boiling point of methanol. The exception is mechanochemical methanolysis shown in entry 11, which proceeds with a small amount of solvent without a catalyst, but this reaction requires mechanical energy equivalent to heating, so it is difficult to compare here.

Table S5. Trailblazing catalytic depolymerizations of PC by methanolysis.^a



Entry	Catalyst	Temp (°C)	Time (h)	BPA (%)	DMC (%)	Solvent	Ref.
1	MO/MCF	125	2.5	97	N.R.	THF/MeOH	29
2	IL/ZnO-NPs	100	7	98	N.R.	THF/MeOH	15
3	CeO ₂ -CaO-ZnO	100	3	90	N.R.	THF/MeOH	14
4	Ammonium Carbonate	75	3	83	N.R.	2-Me-THF/MeOH	17
5	$Zn(HMDS)_2$	70	3	99	N.R.	2-Me-THF/MeOH	28
6	Si-TBD	65	2	96	-	DMC/MeOH	18
7	NaOH	60	0.25	96	100	toluene/MeOH	12
8	Zn complex	50	1	88	N.R.	2-Me-THF/MeOH	21
9	TBD	50	12	88	-	DMC/MeOH	24
10	NaOH	40	0.58	95	N.R.	THF/MeOH	13
11 ^b	wo cat.	-	6	99	N.R.	MeOH	19
12 ^c	Metal Salt	180	0.08	>99	>99	MeOH	27
13	Urea	140	3	100	51	MeOH	20
14	Choline Chloride/Urea DES	130	2.5	99	N.R.	MeOH	25
15	Carbon Nitride	130	10	92	N.R.	MeOH	11
16^{d}	NaOH	120-140	-	90	35	MeOH	22
17	Basic IL	120	1	99	N.R.	MeOH	23
18	Acidic IL	120	3	97	N.R.	MeOH	26
19	Mg ₂ Al-LDH	110	1	98	N.R.	MeOH	30
20	DBU	100	0.52	99	99	MeOH	16
21	$La(acac)_3$	80	8	90	88	MeOH	31
22	La complex	60	8	96	93	MeOH	This Work

^aN. R. indicates "not reported in the literature". ^bBall Milling condition, ^cMicrowave irradiation, ^dContinuous condition.

SI-12 Reference

- 1. M. Saito, T. Ueda, T. Tani, K. Nakamura, US7393982B2, 2008.
- 2. P. C. Andrews, G. B. Deacon, R. Frank, B. H. Fraser, P. C. Junk, J. G. MacLellan, M. Massi, B. Moubaraki,
- K. S. Murray, and M. Silberstein, Eur. J. Inorg. Chem., 2009, 2009, 744.
- 3. Y. Matsushita, K. Sugamoto and T. Matsui, Tetrahedron Letters, 2004, 45, 4723.
- 4. S. Inagaki, K. Saito, S. Suto, H. Aihara, A. Sugawara, S. Tamura, and T. Kawano, *J. Org. Chem.*, 2018, 83, 13834.
- 5. S. N. Hersh, K. Y. Choi, J. Appl. Polym. Sci., 1990, 41, 1033.
- 6. Y. Kim, K. Y. Choi and T. A. Chamberlin, Ind. Eng. Chem. Res., 1992, 31, 2118.
- 7. T. Linderstrom and G. G-. Nordmark, J. Colloid Interface Sci., 1983, 94, 404.
- 8. R. J. Stol and P. L. DE Bruyn, J. Colloid Sci., 1980, 75, 185.
- 9. D. W. J. Osmond, B. Vincent and F. A. Waite, J. Colloid Sci., 1973, 42, 262.
- 10. E. V. Antonakou, D. S. Achilias, Waste Biomass Valor, 2013, 4, 9.
- 11. Y. Xu, Y. Ji, Y. Liu, W. Deng, F. Huang, and F. Zhang, ChemCatChem, 2024, 16, e202301763.
- 12. L.-C. Hub, A. Okua and E. Yamada, Polymer, 1998, 39, 3841.
- 13. F. -S. Liu, Z. Li, S. T. Yu, X. Cui, C. -X. Xie, X. -P. Ge, J. Polym. Environ., 2009, 17, 208.
- 14. F. Liu, Y. Xiao, X. Sun, G. Qin, X. Song, Y. Liu, Chem. Eng. J., 2019, 369, 205.

15. F. Iannonea, M. Casiello, A. Monopolia, P. Cotugnoa, M. C. Sportelli, R. A. Piccaa, N. Cioffia, M. M.

Dell'Annac, A. Naccia, J. Mol. Catal. A. Chemical, 2017, 426, 107.

16. E. Quaranta, D. Sgherza and G. Tartaro, Green Chem., 2017, 19, 5422.

17. P. McKeown, M. Kamran, M. G. Davidson, M. D. Jones, L. A. Román-Ramírez and J. Wood, *Green Chem.*, 2020, **22**, 3721.

18. Z. Fehér, R. Németh, J. Kiss, B. Balterer, K. Verebélyi, B. Iván, J. Kupai, *Chem. Eng. J.*, 2024, **485**, 149832.

19. H. W. Lee, K. Yoo, L, Borchardt and J. G. Kim, Green Chem., 2024, 26, 2087.

20. N. Hu, L. Su, H. Li, N. Zhang, Y. Qi, H. Wang, X. Cui, X. Hou and T. Deng, *Green Chem.*, 2024, **26**, 9378.

- 21. J. M. Payne, M. Kamran, M. G. Davidson and M. D. Jones, ChemSusChem, 2022, 15, e202200255.
- 22. R. Piñero, J. García and M. J. Cocero, Green Chem., 2005, 7, 380.
- 23. M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu and S. Yu, ACS Sustainable Chem. Eng., 2018, 6, 13114.
- 24. T. Do, E. R. Baral, J. G. Kim, Polymer, 2018, 143, 106.
- 25. X. Song, W. Hu, W. Huang, H. Wang, S. Yan, S. Yu, F. Liu, Chem. Eng. J., 2020, 388, 124324.
- 26. J. Guo, M. Liu, Y. Gu, Y. Wang, J. Gao and F. Liu, Ind. Eng. Chem. Res., 2018, 57, 10915.
- 27. C. Alberti and S. Enthaler, Asian J. Org. Chem., 2020, 9, 359
- 28. R. Yang, G. Xu, B. Dong, X. Guo and Q. Wang, ACS Sustainable Chem. Eng., 2022, 10, 9860.
- 29. Y. Zhao, H. Jiang, S. Xue, M. Liu, F. Liu, S. Yu, Solid State Sci., 2020, 107, 106317.
- 30. W. Huang, H. Wang, X. Zhu, D. Yang, S. Yu, F. Liu, X. Song, Appl. Clay Sci., 2021, 202, 105986.
- 31. K. Yamada, N. Komine and M. Hirano, *ChemCatChem*, 2024, 16, e202400870.