

Efficient catalyst removal and recycling in copolymerization of epoxides with carbon dioxide via simple liquid–liquid phase separation

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Supplementary Information

I. General

NMR spectra were recorded on JEOL JNM-ECP500 or JEOL JNM-ECS400 spectrometers. Size-exclusion chromatography analyses were performed with Shodex KF-804L columns using THF as an eluent and the molecular weights were calibrated against standard polystyrene samples. UV-VIS spectra were recorded on SHIMADZU UV-3150 spectrometer. ICP analyses were carried out using Thermo Fisher SCIENTIFIC iCAP 6300 ICP spectrometer.

Propylene oxide (Kanto Chemical) was distilled over CaH₂ under argon prior to use. Complex **1** was synthesized following the literature procedure.¹ Bis(triphenylphosphine)-iminium chloride (Aldrich) was recrystallized from CH₂Cl₂/Et₂O prior to use.

II. Copolymerization Reactions

General Procedure for Table 1 and Table 2, Cycle 1.

Propylene oxide (4.0 mL, 57 mmol) was added to a 50 mL stainless steel autoclave containing complex **1** (9.4 mg, 14 μmol) and bis(triphenylphosphine)iminium chloride (4.2 mg, 7.2 μmol) under argon. This was pressurized with CO₂ (2.0 MPa) and the mixture was stirred for 13 h at 22 °C. After removal of the remaining CO₂, the reaction mixture was transferred to a vial with CH₂Cl₂ and concentrated under vacuum. The residue was dissolved in CH₂Cl₂ (6.0 mL) and carboxylic acid (28 μmol) was added to it. The mixture was stirred for 2 h at room temperature and the solvent was removed under vacuum. This was dissolved in MeCN (10 mL) and extracted with hexane (20 mL x 3). The hexane phase was concentrated and the amount of cobalt complex was estimated by UV-VIS spectroscopy in CH₂Cl₂. The MeCN phase was concentrated to afford poly(propylene carbonate), which was analyzed by ¹H NMR in CDCl₃ and by size-exclusion chromatography in THF.

General Procedure for Table 2, Cycles 2–6.

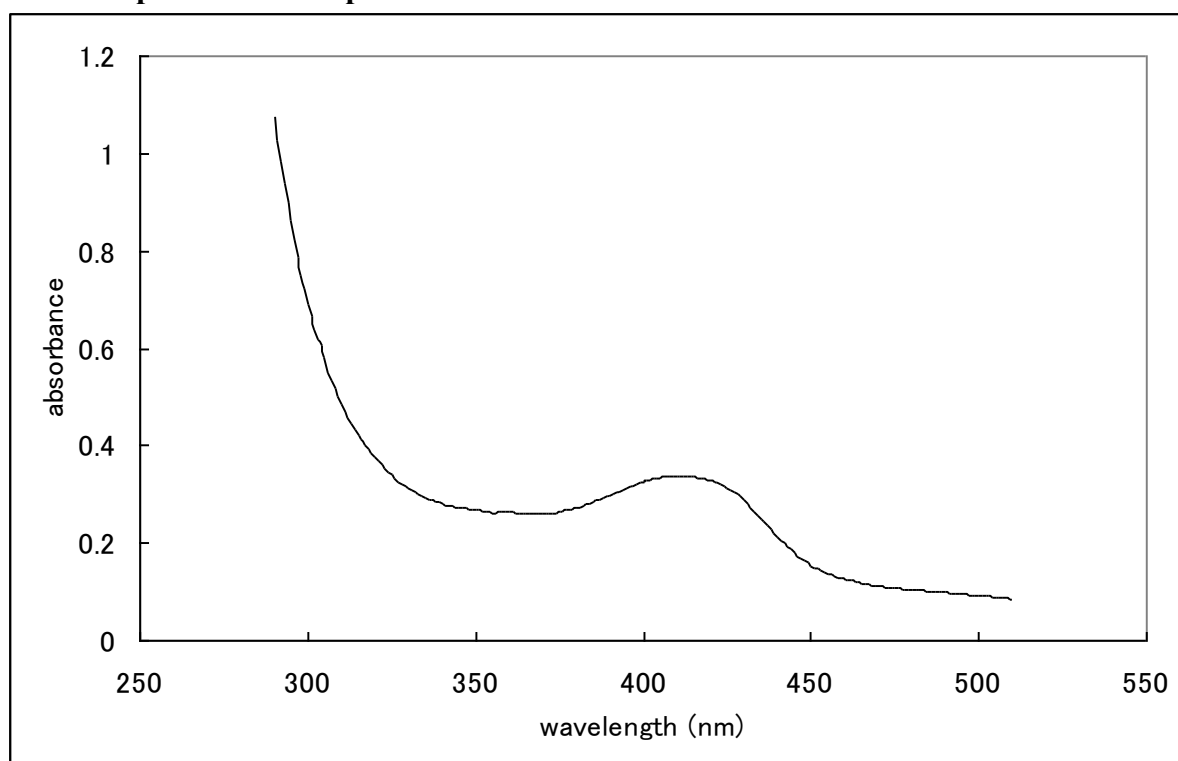
The recovered cobalt complex from the hexane phase was dried under vacuum (0.06 Torr) for 1 h at room temperature in an 80 mL glass Schlenk tube. This was then dissolved in 1000 equiv of propylene oxide (0.96–0.78 mL) and transferred into a 50 mL stainless steel autoclave containing bis(triphenylphosphine)iminium chloride (0.5 equiv to cobalt) under argon. The Schlenk tube was washed with propylene oxide (1000 equiv x 3) and this was also

¹ M. Tokunaga, J. F. Larrow, F. Kakiuchi and E. N. Jacobsen, *Science* 1997, **277**, 936.

transferred into the autoclave. The autoclave was pressurized with CO₂ (2.0 MPa) and the mixture was stirred for 13 h at 22 °C. After removal of the remaining CO₂, the reaction mixture was transferred to a vial with CH₂Cl₂ and concentrated under vacuum. The residue was dissolved in CH₂Cl₂ (6.0 mL) and myristic acid (2.0 equiv to cobalt) was added to it. The mixture was stirred for 2 h at room temperature and the solvent was removed under vacuum. This was dissolved in MeCN (10 mL) and extracted with hexane (20 mL x 3). The hexane phase was concentrated and the amount of cobalt complex was estimated by UV-VIS spectroscopy in CH₂Cl₂. The MeCN phase was concentrated to afford poly(propylene carbonate), which was analyzed by ¹H NMR in CDCl₃ and by size-exclusion chromatography in THF.

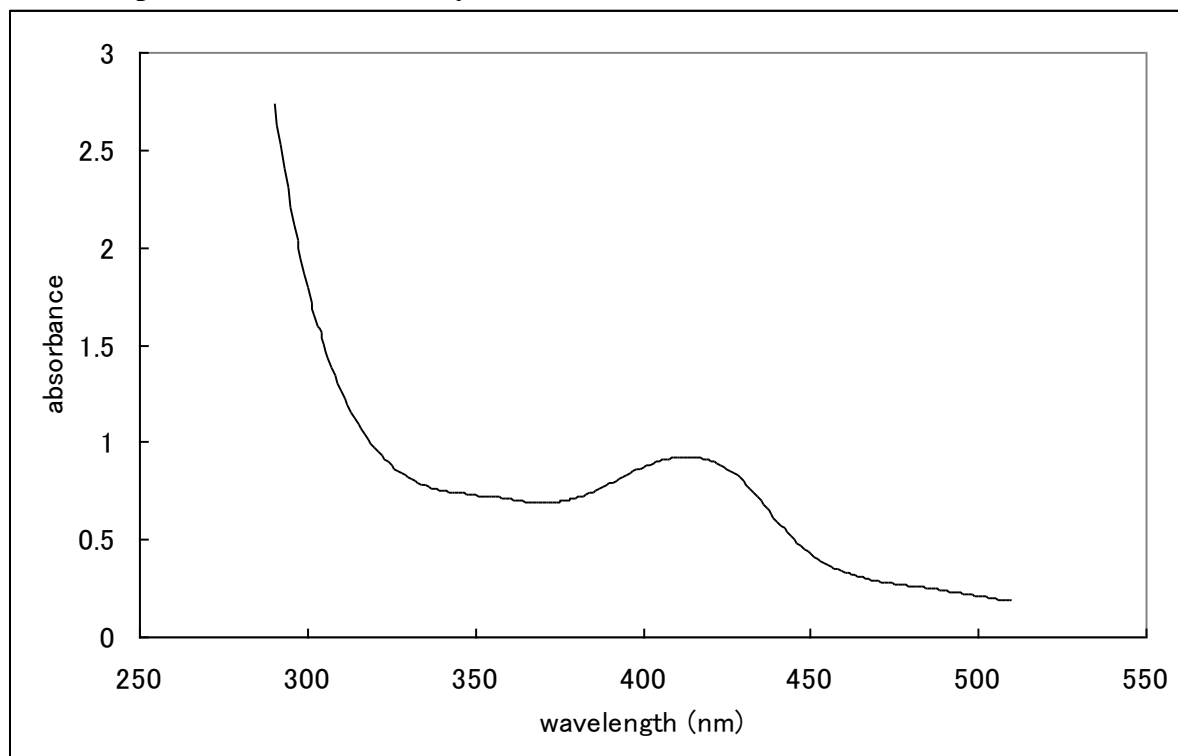
III. Representative UV-VIS and ¹H NMR Spectra

UV-VIS Spectra for Complex 1.



Complex **1** (16.8 mg, 25.3 μmol) was dissolved in CH₂Cl₂ to make a 500 mL solution ($c = 5.07 \times 10^{-5}$ M). The absorbance A at λ_{max} (411 nm) was determined to be 0.338 using a cell having optical path length $l = 1.00$ cm. Based on $A = \epsilon \cdot c \cdot l$, ϵ was calculated to be 6.67×10^3 M⁻¹·cm⁻¹.

UV-VIS Spectra for Table 1, entry 4.



The residue of the hexane phase was dissolved in CH_2Cl_2 to make a 100 mL solution. The absorbance A at λ_{max} (411 nm) was determined to be 0.927 using a cell having optical path length $l = 1.00$ cm. Based on $A = \epsilon \cdot c \cdot l$ and assuming $\epsilon = 6.67 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, c was calculated to be 1.39×10^{-4} M. This led to the estimated amount of removed cobalt being $13.9 \mu\text{mol}$, which corresponded to 96% of the used complex **1** (9.6 mg, $14.5 \mu\text{mol}$).

^1H NMR for Poly(propylene carbonate) in CDCl_3 .

