Supporting Information

Small Number of Active Sites and Single-Locus Kinetics Revealed in (salph)Co-Catalyzed Ethylene Oxide Polymerization

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I. General information

Ethylene oxide was purchased from Sigma Aldrich in a lecture bottle. The complex \((\text{salph}^{\text{Bu}})\text{CoOAc} \quad (N,N'\text{-bis-(3,5-di-tert-butylsalicylidene)}-1,2\text{-phenylenediaminocobalt acetate})\) (1) was synthesized according to literature procedure.\(^1\) Crystals of catalyst \((\text{salph}^{\text{Bu}})\text{CoOMe} \quad (\text{methoxy} \quad N,N'\text{-bis-(3,5-di-tert-butylsalicylidene)}-1,2\text{-phenylenediaminocobalt})\) (2) were obtained by a generous sharing from Prof. Geoffrey W. Coates.

II. Construction of Gas-Tight Reaction Cells for Microscopy

Bottoms of screw cap dram vials (17 mm x 60 mm, VWR Scientific) were sheared off by UCI scientific glassblower Jorg Meyer leaving a flat bottom cylinder with screw cap. To assemble the reaction cells these hollow cylinders with screw caps were attached to the glass coverslips (25 x 25 mm\(^2\), No. 1.5, VWR Scientific) with a thickness of 0.17 mm by applying epoxy (5 Minute Epoxy, Devcon) to the outside base of the tubes. The MSDS of our epoxy characterizes it as cross-linked bisphenol A diglycidyl ether; thus it does not contain amines for offgassing. The epoxy resin was put on the outside of vial, not inside, and further the crystals were added and the vial was flushed with ethylene oxide immediately prior to data acquisition. All completed cells (Figure S1) were covered and stored for use the following day.
III. Reaction Procedure of Ethylene Oxide Polymerization with (salph)CoOR (R = Ac, 1; R = Me, 2) Catalyst

For the imaging experiment, in a fume hood, (salph)CoOR catalyst (R = Ac, 1; R = Me, 2) (2 mg, 0.003 mmol) was added to a clean reaction cell constructed with a screw-thread dram vial. The vial then was capped with a polypropylene screw cap with a PTFE/Silicone resealable septum (VWR Scientific). Ethylene oxide gas was added to the reaction cell and the cell was wrapped with electric tape to minimize any gas leakage (Figure S2). Caution: ethylene oxide is highly toxic and needs to be handled according to safe procedures.
c.

**Figure S2.** Photographs of sample preparation for ethylene oxide gas-phase polymerization reaction. (a) Catalyst 1 in a reaction cell sealed with a septum cap was exposed to ethylene oxide gas. (b) Expansion. (c) The reaction cell containing catalyst 1 and ethylene oxide gas was wrapped with electric tape before transferring to the microscope for imaging.

**IV. Microscopy and General Parameters**

Image acquisition was performed using two different microscope configurations: top lighted (shadow) and bottom lighted (reflection) (Figure S3). A schematic of the top lighted microscopy setup is shown in Figure S3a below. Widefield imaging was performed with a IX71 inverted microscope (Olympus Corporation) and an oil immersion objective with a 1.45 numerical aperture. Samples were illuminated with a flashlight positioned on the opposite side of the sample then the detector. Samples were imaged with a C9100-13 electron multiplier CCD camera (Hamatsu Photonics). The CCD chip was a back-thinned electron multiplication type with an effective $512 \times 512$ array of pixels. The SlideBook software package (Intelligent Imaging) was configured to acquire continuous images with 300 ms per frame. The time-lapse images were initially recorded by the SlideBook software as Shockwave Flash Objects and were converted by the same software to TIFF files. Images were viewed in ImageJ (NIH, [http://rsbweb.nih.gov/ij/](http://rsbweb.nih.gov/ij/)).
InVia Rennishaw Raman Microscope was used for bottom lighted microscopic observations. An air objective (20x) lighted the sample with a white light source and the image was recorded by a Phillips SPC1030NC webcam. Images 417 x 308 µm² were acquired by means of Snapshot Maker software taking pictures from the camera image every 5 s. A schematic of this experimental setup is shown in Figure S3b.

Figure S3. Sketches of microscope setups. (a) Illumination above sample; (b) illumination same side as sample signal detection (reflection).

V. Image Acquisition of Ethylene Oxide Polymerization with (salph)CoOR (R = Ac, 1; R = Me, 2) Catalyst on Top Lighted Microscope

The sample was removed from the fume hood and mounted on the microscope objective using a drop of immersion oil (n = 1.516, Olympus) and illuminated with a lamp. Individual crystals of 1 or 2 were located on the surface. After satisfactory focus was achieved, image acquisition was then started and images were taken every 30 s with 300 ms exposure time for 24 h. A gas/solid-phase real-time polymerization of ethylene oxide with catalyst 1 was captured (see manuscript, Figure 1).
VI. Image Acquisition of Ethylene Oxide Polymerization with (salph)CoOR (R = Ac, 1; R = Me, 2) Catalyst on Bottom Lighted Microscope

The sample was removed from the fume hood and mounted on the microscope stage upside down (some crystals reproducibly remained stuck to the glass while upside down) due to the microscope geometrical configuration (Figure S4). Individual crystals of 2 were located with a 5x objective and after focusing observed on a 20x objective. Images were then taken every 5 s with screenshot software Snapshot Maker.

![Figure S4. Photo of bottom lighted microscope.](image)

VII. Raman Spectroscopy

Raman measurements were performed on inVia Rennishaw Raman Microscope using 532 nm laser excitation, 5% laser power (2.25W), 10 s exposure time and 50% laser focus. Low laser power was used to prevent thermal decomposition of the sample.
Wide range of wave vectors was scanned from 100 to 3200 cm\(^{-1}\). Commercial software (WIRE 3.2) was used to process spectral data, which were obtained in one accumulation. Spectra were compared to those of ethylene oxide and polyethylene oxide reported in literature.\(^2\)^\(^3\) Raman spectrum of commercially available PEO was obtained at 100% laser power (45W), 15 s exposure and 50% laser focus to assure the alignment of the instrument (Figure S5).

![Raman spectrum of commercially available PEO](image)

**Figure S5.** Raman spectrum of commercially available PEO, acquired for comparison.

**VIII. Data analysis**

Analysis of pictures obtained from ScreenMaster software was digitized in Adobe Photoshop CS6 software. Prior to digitization, snapshots (full stack within one experiment) were cropped to the region corresponding to the webcam output and levels were adjusted to increase contrast. Surface area was calculated by setting scale, selecting the darkened region of interest with the “selection tool” and recording the number of pixels.
