Supplementary Material for:

Biologically Synthesized or Bioinspired Process-Derived Iron Oxides as Catalysts for Living Cationic Polymerization of Vinyl Ether

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References
Experimental Section

Materials  IBVE (TCI; >99.0%), ethyl acetate (Wako; >99.5%), and heptane (Nacalai Tesque; >99.0%) were distilled twice over calcium hydride before use. 1,4-Dioxane (Wako; >99.5%) was distilled over calcium hydride and then lithium aluminum hydride. Toluene (Wako; 99.5%) was dried using solvent purification columns (Glass Contour). An adduct of IBVE with HCl [CH₃CH(OiBu)Cl; IBVE–HCl] was prepared from the addition reaction of IBVE with HCl.¹ A commercially available α-Fe₂O₃ (Aldrich; 99+%; the crystal structure was determined by powder X-ray diffraction) was used after crushing with a mortar. nBu₄NCl (Fluka; >99.0%) was used without further purification.

The Isolation and Purification of Bacterial Fe₃O₄  Magnetotactic bacteria, Magnetospirillum magneticum strain AMB-1 (ATCC700264), were microaerobically grown in an 8-liter fermenter as described previously.² After 7 days of cultivation, the cells were harvested by centrifugation and disrupted using a French press (1100 kg/cm²). The bacterial Fe₃O₄ from the disrupted cells was then collected using a neodymium boron magnet and washed 10 times with HEPES buffer (pH 7.0). The organic components surrounding the bacterial Fe₃O₄ were removed by treating the Fe₃O₄ 3 times with 1% (w/v) SDS in a 100 °C water bath for 30 min.³ During this process, the sample was treated briefly in an ultrasonic bath. The obtained Fe₃O₄ was then washed with HEPES buffer, ethanol, and toluene. After washing, the Fe₃O₄ was dried in air for 1 day. Before use, the Fe₃O₄ was heated at 100 °C under reduced pressure for 10 min to remove loosely adsorbed water.

The Synthesis and Characterization of Iron Oxide via a Microbial-Mineralization-Inspired Process  An aqueous solution containing 25 mM of disodium dihydrogen ethylenediamine tetraacetate (EDTA, Kanto; 99.5 %) was prepared in a polypropylene vessel using purified water. Then, 25 mM of iron chloride tetrahydrate (FeCl₂·4H₂O, Kanto 99.0 %) was dissolved in 100 mL of the aqueous EDTA solution. The pH of the aqueous solution containing EDTA and FeCl₂ was adjusted to 11 using 10 M of NaOH (Junsei 96.0 %) aqueous solution. The precursor solutions were maintained at 90 °C for 1 day without stirring. The precipitates were centrifuged and washed with purified water. Then, the resultant powder was dried at 60 °C. The crystal phase was identified using powder X-ray diffraction (XRD, Rigaku MiniFlex II, Cu-Kα radiation equipped with a graphite monochromator). Fourier-transform infrared (FT-IR) absorption spectroscopy (Bruker, Alpha-T) was also used to confirm the crystal phase. The FT-IR spectra were obtained using the KBr method. The sample morphologies were observed using a field-emission scanning electron microscope (FESEM, FEI Sirion) and a field-emission transmission electron microscope (FETEM, FEI Tecnai F20 operated at 200 kV). The specific surface area was calculated by...
the BET method using nitrogen adsorption isotherms obtained at 77 K (Micromeritics, TriStar 3000). Before measuring the specific surface area, the samples were dried under vacuum at 60 °C for 5 h.

Thermogravimetric analysis (TG, Seiko TG-DTA 6200) was performed under air atmosphere to estimate the amount of the adsorbed water and hydroxyl groups on the surface of the iron oxides. About 5–10 mg of the specimen powder was put in a platinum pan. Then, the temperature was rose from room temperature to 1000 °C by °C the rate of temperature increase set at 5 °C min⁻¹.

**Polymerization Procedures** The following is a typical polymerization procedure (the Fe₃O₄ system is used as an example). A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blower temperature was ~450 °C) under dry nitrogen for 8 min. Fe₃O₄ (3 mg; 1 × 10⁻² mmol) was loaded into the tube in air and heated with the heat gun under reduced pressure for 10 min. The heating temperature was controlled by maintaining a suitable distance between the heat gun and the bottom of the tube. The temperature was monitored using a Peltier-type thermometer (Custom; CT-800WP and LK-800WP). After the tube was purged with N₂ and cooled to room temperature, toluene (1.68 mL), heptane (0.12 mL), 1,4-dioxane (0.20 mL; 2.3 mmol), and IBVE (0.25 mL; 1.9 mmol) were successively added into the tube using dry syringes. The polymerization was initiated by the addition of a pre-chilled 40 mM IBVE-HCl solution (0.25 mL; 1.0 × 10⁻² mmol) in toluene at 0 °C. During the polymerization, the heterogenous reaction mixture was magnetically stirred using a small, handmade stirring bar constructed from a thin glass tube and a wire. A small amount (~0.05 mL) of the reaction mixture was extracted several times during the reaction to determine the degree of monomer conversion from the residual concentration of IBVE, which was measured using gas chromatography with heptane (5 vol%) as an internal standard. The reaction was finally terminated through the addition of pre-chilled methanol that contained a small amount of an aqueous ammonia solution. The catalyst was removed using a magnet (in reactions using α-Fe₂O₃, the catalyst was separated by centrifugation and decantation). The polymer product was obtained by evaporating the remaining toluene, 1,4-dioxane, and IBVE.

For experiments examining the reuse of the catalyst, the separated iron oxides were successively washed with acetone, ethanol, acetone, and hexane. After washing, the iron oxides were dried in air for a few days. The oxides were heated at a determined temperature under reduced pressure immediately before the 2nd polymerization.

Two different lots of Fe₃O₄ were used for the experiments: the first lot corresponds to entry 1 in Table 1, Figures 2 and S2, and the second lot corresponds to entries 2–5 in Table 1. In addition, two different lots of α-Fe₂O₃ were used: the first lot corresponds to entries 6–8 in Table 1, Figures 3, 4, and S10, and the second lot corresponds to Figures S5 and S11.
Characterization of Polymers  The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns [TSK gel G-4000HXL, G-3000HXL, and G-2000HXL; exclusion limit molecular weight = 4 × 10^5, 6 × 10^4, and 1 × 10^4, respectively; bead size = 5 mm; column size = 7.8 mm (internal diameter) × 300 mm; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (\(M_n\)) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (\(M_w/M_n\))] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; \(M_n = 577–1.09 \times 10^6, M_w/M_n \leq 1.1\)). Nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500.16 MHz for \(^1\)H and 125.77 MHz for \(^{13}\)C).

Analysis of Iron Oxides after Heat-Treatment  After the thermal treatment, the XRD patterns, FT-IR spectra, and specific surface area were measured using the same methods as those before the thermal treatment.
Fig. S1  BET surface area analysis of microbial-mineralization-inspired process-derived α-Fe₂O₃ and commercially available α-Fe₂O₃.

Fig. S2  $M_n$ and $M_w/M_n$ for the polymerization using fresh or reused Fe₃O₄ ([IBVE]₀ = 0.76 M, [IBVE–HCl]₀ = 4.0 mM, [Fe₃O₄] = 0.7 mol% to IBVE, [1,4-dioxane] = 1.0 M, in toluene at 0 °C; see Figure 2 for time–conversion curves and MWD curves)
Fig. S3  $^1$H NMR spectra of poly(IBVE)s obtained with (A) a bacterial Fe$_3$O$_4$ and (B) a microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ (in CDCl$_3$ at 30 ºC; analyzed sample: (A) entry 1 and (B) entry 6 in Table 1).

Fig. S4  $^{13}$C NMR spectra of poly(IBVE)s obtained with (A) a bacterial Fe$_3$O$_4$ and (B) a microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ (the peaks of the main chain methylene carbons; in CDCl$_3$ at 30 ºC; analyzed sample: (A) entry 1 and (B) entry 6 in Table 1).
Fig. S5  (A) Time–conversion curves and (B) $M_n$ and $M_w/M_n$ for the polymerization of IBVE using microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ ([IBVE]$_0$ = 0.76 M, [IBVE–HCl]$_0$ = 4.0 mM, [$\alpha$-Fe$_2$O$_3$] = 0.7 mol% to IBVE, [1,4-dioxane] = 1.0 M, in toluene at 0 ºC).

Fig. S6  XRD patterns of microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ heated at 100, 200, or 300 ºC [(A) whole region, (B) enlarged view for comparing half widths].
Fig. S7  BET surface area analysis of microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ heated at 100, 200, or 300 °C (N$_2$ adsorption).

<table>
<thead>
<tr>
<th>Heating-temperature</th>
<th>Specific area (m$^2$g$^{-1}$)</th>
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<tr>
<td>300 °C</td>
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<tr>
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Fig. S8  IR spectra of microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ after heat-treatment (Note: The iron oxides for IR spectrometric analysis were mixed with KBr under air. A part of the OH absorptions may have been attributed to water adsorbed during the preparation step).
Fig. S9  Thermogravimetric analysis of microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ (the weight loss is probably attributed to the removal of chemically and/or physically adsorbed water molecules).

Fig. S10  Time–conversion curves for the polymerization of IBVE using microbial-mineralization-inspired process-derived $\alpha$-Fe$_2$O$_3$ or commercial $\alpha$-Fe$_2$O$_3$ in the presence of a small amount of $n$Bu$_4$NCl ($[\text{IBVE}]_0 = 0.76$ M, $[\text{IBVE–HCl}]_0 = 4.0$ mM, $[\alpha$-Fe$_2$O$_3]$ = 0.7 mol% to IBVE, $[1,4$-dioxane] = 1.0 M, $[n$Bu$_4$NCl]$_0 = 0$, 0.01, 0.05, or 0.1 mM, in toluene at 0 ºC; the iron oxides were heated at ~300 ºC under reduced pressure for 10 min before use).

Note: The chloride anion derived from $n$Bu$_4$NCl functions as a strong Lewis base and deactivates the active sites on the iron oxides. As shown in Fig. S10, the polymerization using the synthesized $\alpha$-Fe$_2$O$_3$ proceeded in the presence of 0.05 mM of $n$Bu$_4$NCl but that using the commercially available $\alpha$-Fe$_2$O$_3$ obviously retarded even with 0.01 mM of $n$Bu$_4$NCl. The results suggest that the amount of the active sites of the synthesized oxide was roughly estimated to be more than five times larger than that of the commercial oxide.
Fig. S11  (A) Time–conversion curves and (B) $M_n$ and $M_n/M_n$ for the polymerization of IBVE using microbial-mineralization-inspired process-derived $\alpha$-$\text{Fe}_2\text{O}_3$ or commercial $\alpha$-$\text{Fe}_2\text{O}_3$ ([IBVE]$_0$ = 0.76 M, [IBVE–HCl]$_0$ = 4.0 mM, [α-Fe$_2$O$_3$] = 0.7 mol% to IBVE, [1,4-dioxane] = 1.0 M, in toluene at 0 °C; the iron oxides were heated at ~300 °C under reduced pressure for 10 min before use).
References

