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### **Supporting Information**

### Ultrahigh Oxygen-Scavenging Norbornene Copolymers Bearing Imidazolyl Iron Complex for Fabricating Active and Sustainable Packaging Films

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1. Materials

Iron(II) *N*,*N*'-bis(salicylidene)ethylenediamine) (Fe(II)salen), cobalt(II) naphthenate, 2-norbornene, 5-ethylidene-2-norbornene, 5-norbornene-2-carboxylic acid, 4-(4,6dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM), methyl linoleate (ML), and 1-benzylimidazole (bim) were purchased from Tokyo Chemical Industry. 1-(2-Hydroxyethyl)imidazole and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) (Grubbs 2nd catalyst) were purchased from Sigma-Aldrich. All reagents were used without further purification prior to use.

#### 2. Synthesis of 5-norbornene-2-yl-carboxyethyl-1-imidazole (N-im)



5-Norbornene-2-yl-carboxyethyl-1-imidazole was synthesized by a modified version of a previously reported method.<sup>1-2</sup> Ten grams (0.075 mol) of 5-norbornene-2-carboxylic acid and 12.0 g (0.11 mol) of 1-(2-hydroxyethyl)imidazole in 500 mL of THF were stirred with 41.5 g (0.11 mol) of DMT-MM at room temperature for 5 h. The solvent was then

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removed, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O and purified using silica gel column chromatography with acetone as the eluent, which afforded a yellow oil (yield: 6.5 g, 52 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.53(s, 1H, H<sub>j</sub>), 7.07(s, 1H, H<sub>i</sub>), 6.97(s, 1H, H<sub>h</sub>), 6.17(dd, *J* = 6.0, 3.0 Hz,1H, H<sub>a</sub>(exo)), 6.15(dd, *J* = 6.0, 3.0 Hz,1H, H<sub>a</sub>(endo)), 6.13(dd, *J* = 6.0, 3.0 Hz,1H, H<sub>a</sub>'(endo)), 5.78 (dd, *J* = 6.0, 3.0 Hz,1H, H<sub>a</sub>'(exo)), 4.34 (t, *J* = 4.5 Hz, 1H, H<sub>g</sub>), 4.27 (t, *J* = 5.5 Hz, 1H, H<sub>f</sub>), 4.20(t, *J* = 5.5 Hz, 1H, H<sub>f</sub>), 4.17 (t, *J* = 4.5 Hz, 1H, H<sub>g</sub>), 3.16-3.03 (s, 1H, H<sub>b</sub>'), 3.02-2.88(m, 2H, H<sub>b</sub>, H<sub>e</sub>), 2.27(dt, *J* = 9 Hz, 1.5 Hz 1H, H<sub>e</sub>), 1.88(m, 1H, H<sub>d</sub>), 1.37(m, 3H, H<sub>d</sub>, H<sub>c</sub>). FAB-MS m/z: [M]<sup>+</sup> 233.0. calcd 233.1. Anal. calcd for C<sub>13</sub>N<sub>2</sub>H<sub>16</sub>O<sub>2</sub>: C 69.4, H, 4.2; found: C 69.0, H 4.1.

#### 3. Polymerization of norbornene and 5-ethylidene-2-norbornene

Norbornene (4.7 g, 50 mmol) in 400 mL of THF and 50 µmol of Grubbs 2nd catalyst in 50 mL of THF were combined and stirred at room temperature for 5 h, then poured into 5 L of methanol. The precipitate was filtered off, washed with methanol, and resolved in THF, and the solution was poured again into methanol. The resulting white powder was filtered off and dried under vacuum overnight. Yield: 4.2 g, 90 %. <sup>1</sup>H-NMR of PN (CDCl<sub>3</sub>- $d_1$ ,  $\delta$ ): 5.30 (s, 1H, H<sub>a</sub> (exo)), 5.18 (s, 1H, H<sub>a</sub> (endo)), 2.92 (s, 1H, H<sub>b</sub>), 2.40 (s, 1H, H<sub>b</sub>), 1.90-1.72 (br, 3H, H<sub>c</sub>, H<sub>d</sub>), 1.40 (s, 2H, H<sub>d</sub>), 1.00 (m, 1H, H<sub>c</sub>).  $M_n = 2.5 \times 10^5$ ,

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 $M_{\rm w}/M_{\rm n} = 1.4$ . Poly(5-ethylidene-2-norbornene) (PEN) was synthesized by the same procedure, and with the same molar ratio. <sup>1</sup>H-NMR of PEN (CDCl<sub>3</sub>,  $\delta$ ): 5.43-5.11 (m, 3H, H<sub>a</sub>, H<sub>e</sub>), 3.28-3.02 (m, 1H, H<sub>b</sub>), 3.00-2.81 (m, 1H, H<sub>b</sub>), 2.67-1.74 (br, 6H, H<sub>c</sub>, H<sub>d</sub>, H<sub>f</sub>), 1.16 (m, 1H, H<sub>c</sub>). Yield: 4.5 g, 75 %.  $M_{\rm n} = 1.2 \times 10^5$ ,  $M_{\rm w}/M_{\rm n} = 1.7$ .



# 4. Copolymerization of norbornene and 5-norbornene-2-yl-carboxyethyl-1imidazole

2-Norbornene (4.7 g, 50 mmol) and 110.6 mg (0.5 mmol) of 5-norbornene-2-ylcarboxyethyl-1-imidazole in 200 mL of THF were combined with 42.5 mg (50  $\mu$ mol) of Grubbs 2nd catalyst in 50 mL of THF and stirred at room temperature for 10 h. The reaction mixture was then poured into 5 L of methanol, and the precipitate was dissolved in THF and re-precipitated with methanol. The resulting white powder was dried in a vacuum oven overnight. <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): from PN, 5.34 (s, 1H, H<sub>a</sub> (exo)), 5.20 (s, 1H, H<sub>a</sub>(endo)), 2.78 (s, 1H, H<sub>b</sub>), 2.43 (s, 1H, H<sub>b</sub>), 1.90-1.72 (br, 3H, H<sub>c</sub>, H<sub>d</sub>), 1.34 (s, 2H, H<sub>d</sub>), 1.01 (m, 1H, H<sub>c</sub>); from residual 5-norbornene-2-yl-carboxyethyl-1-imidazole,

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7.53(s, 1H, H<sub>j</sub><sup>,</sup>), 7.07(s, 1H, H<sub>i</sub><sup>,</sup>), 6.97(s, 1H, H<sub>h</sub><sup>,</sup>), 6.15-6.09(m, 1H, H<sub>a</sub><sup>,</sup>), 5.78(m, 1H, H<sub>a</sub><sup>,</sup>), 4.27-4.20(m, 4H, H<sub>f</sub><sup>,</sup>, H<sub>g</sub><sup>,</sup>), 3.16-3.03 (s, 1H, H<sub>b</sub><sup>,</sup>), 3.02-2.88(m, 2H, H<sub>b</sub><sup>,</sup> H<sub>e</sub><sup>,</sup>), 2.27(m, 1H, H<sub>e</sub><sup>,</sup>), 1.88(m, 1H, H<sub>d</sub><sup>,</sup>), 1.37(m, 3H, H<sub>d</sub><sup>,</sup>, H<sub>c</sub><sup>,</sup>).



## 5. Copolymerization of 5-ethylidene-2-norbornene and 5-norbornene-2-ylcarboxyethyl-1-imidazole

2-Norbornene (6.0 g, 50 mmol) and 127.8 mg (0.5 mmol) of 5-norbornene-2-ylcarboxyethyl-1-imidazole in 50 mL of THF were combined with 42.5 mg (50  $\mu$ mol) of Grubbs 2nd catalyst in 20 mL of THF and stirred at room temperature for 24 h. The reaction was then poured into 5 L of methanol, and the re-precipitated product was purified with methanol. The resulting white powder was dried in a vacuum oven overnight. <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): from PEN, 5.43-5.11 (m, 3H, H<sub>a</sub>, H<sub>e</sub>), 3.28-3.02 (m, 1H, H<sub>b</sub>), 3.00-2.81 (m, 1H, H<sub>b</sub>), 2.67-1.74 (br, 6H, H<sub>c</sub>, H<sub>d</sub>, H<sub>f</sub>), 1.16 (m, 1H, CH<sub>2</sub> H<sub>c</sub>); from residual 5-norbornene-2-yl-carboxyethyl-1-imidazole, 7.53(s, 1H, H<sub>j</sub><sup>,</sup>), 7.07(s, 1H, H<sub>i</sub><sup>,</sup>), 6.97(s, 1H, H<sub>h</sub><sup>,</sup>), 6.15-6.09(m, 1H, H<sub>a</sub><sup>,</sup>), 5.78(m, 1H, H<sub>a</sub><sup>,</sup>), 4.27-4.20(m, 4H, H<sub>f</sub>, H<sub>g</sub><sup>,</sup>),

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3.16-3.03 (m, 1H, H<sub>b</sub><sup>'</sup>), 3.02-2.88(m, 2H, H<sub>b</sub><sup>'</sup>, H<sub>e</sub><sup>'</sup>), 2.27(m, 1H, H<sub>e</sub><sup>'</sup>), 1.88(m, 1H, H<sub>d</sub><sup>'</sup>),

1.37(m, 3H, H<sub>d'</sub>, H<sub>c'</sub>).



P(EN-im)

The compositions of the copolymers were estimated according to the <sup>1</sup>H-NMR spectra (Fig. S1, S2, Table S1). The content of 5-norbornene-2-yl-carboxyethyl-1-imidazole in the copolymers was slightly lower than the feed ratio, which may be attributed to its lower reactivity compared with that of 2-norbornene or 5-ethylidene-2-norbornene. Especially, for PEN-im, steric hindrance between the ethylidene and imidazole groups in the side chain may cause a lower reactivity.

#### 6. Film fabrication

The polymer films were prepared by casting their solutions. PEN-im (63.7 mg, 530  $\mu$ mol) was dissolved completely in toluene to obtain the 2 wt% solution. Fe(II)salen (0.58 mg, 1.8  $\mu$ mol) was dissolved in toluene (1 mL) under a nitrogen atmosphere to prepare a

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complex solution. Then, ML was added to the solution under stirring. The composition of the Fe(II)salen/ML/PEN-im film was 1.8/27/530 (molar ratio for the PEN-im repeating unit). Once the solution was well mixed, it was poured into a Teflon Petri dish (50 mm in diameter) and kept under nitrogen flow for one day to evaporate the toluene. Then, the films were stored under vacuum at ambient conditions to completely remove any residual solvent. The PN-im film was prepared by the same method and with the same molar ratio. For the PEN and PN films, PEN or PN, Fe(II)salen, and bim were dissolved completely in toluene under stirring in a glass bottle under a nitrogen atmosphere. Then, ML was added to the solution under stirring. The composition of the Fe(II)salen-bim/ML/PN and PEN films was 1.8/27/530 (molar ratio for the PEN or PN repeating unit). Fabrication of the 1,2-PB film followed our previous report.<sup>3</sup>

#### 7. Oxygen consumption measurement

Oxygen consumption was measured using gas chromatography (C-R8A, Shimadzu). Glass flasks (1 L, initial oxygen amount: 210 mL) were used as containers for the oxygen scavengers (polymer films or commercially available iron powders, oxygen scavenging sachets, Mitsubishi Gas Chemicals, Ageless). The film specimen was placed inside the glass beaker, which was subsequently sealed and placed in a temperature-controlled room at 30 °C for the duration of the oxygen-scavenging experiment. Oxygen consumption (O<sub>2</sub>

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gas volume at STP/g(film)) was calculated by periodically monitoring the decreased oxygen amount in the flask. To minimize the influence of polymer mass and thickness on the oxygen uptake measurements, all of the polymer films had the same surface area and similar thicknesses (25  $\mu$ m). To eliminate the influence of negative pressure inside the bottle used for the oxygen consumption measurement, time courses of oxygen consumption for film specimens with different sizes under an air atmosphere were measured at room temperature (**Fig. S7**). A correlation was confirmed in the range where the film area or weight was less than 40 cm<sup>2</sup> with a thickness of 25  $\mu$ m or the film mass was 102 mg to negate any negative pressure influence on the oxygen-scavenging capacity measurements.

#### 8. Other measurements

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a JEOL ECX-500 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Mass, FT-IR, UV-vis, and X-ray photoelectron spectra were measured using a JMS-GCMATE II or Bruker Daltonics Autoflex, JASCO FT-IR-6100, JASCO V-550, and JEOL 9010TR spectrophotometer, respectively. Inductively coupled plasma optical emission

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spectroscopy was performed to monitor the amounts of iron and cobalt eluted into water (ICP-OES 5100, Agilent). SEM images (accelerating voltage of 15 kV) were obtained using a field emission scanning electron microscope (S-4500, Hitachi). Oxygen and nitrogen gas permeabilities through the films were measured with a low-vacuum downstream method using a gas permeability measurement system (K-315N-01, Tsukuba Rikaseiki).



**Fig. S1** <sup>1</sup>H-NMR (500 MHz,  $CHCl_3-d_1$ ) spectrum of poly(norbornene-5ethylidene-2-norbornene-2-yl-carboxyethyl-1-imidazole (PN-im)).



**Fig. S2** <sup>1</sup>H-NMR (500 MHz,  $CHCl_3-d_1$ ) spectrum of poly(5-ethylidene-2-norbornene-5-norbornene-2-yl-carboxyethyl-1-imidazole (PEN-im)).



**Fig. S3** Visible transmittance of the PEN-im/Fe(II)salen film before and after oxygen exposure for one month.



Fig. S4 Photographs of the PEN-im/Fe(II)salen film.



**Fig. S5** Cross-sectional SEM image (a) and Fe mapping (b) of the PENim/Fe(II)salen film. Cross-sectional SEM image (c) and Fe mapping (d) of the PEN-im/Fe(II)salen film after air exposure for one month.



**Fig. S6** Consumption yield of unsaturated of unsaturated hydrocarbons in the polymers through air exposure.  $\bigcirc$ : PEN-im;  $\bigcirc$ : PEN;  $\blacksquare$ : PN-im;  $\Box$ : PN.



**Fig. S7** Oxygen consumption of the PEN-im/Fe(II)salen film specimen after one month in a 1-L glass beaker.



**Fig. S8** IR spectra of the PEN-im/Fe(II)salen film before (black) and after (red) air exposure for one month.



**Fig. S9** Solid-state <sup>13</sup>C-NMR spectra of the PEN-im/Fe(II)salen film before (black) and after (red) air exposure for one month. Signals for carbon connected to oxygen by a single bond (e.g., ethers), carboxylic carbons, and carbonyl carbons (in saturated ketones) are labeled A–C, respectively.



**Fig. S10** X-ray photoelectron spectra of the PEN-im/Fe(II)salen film before (black) and after (red) air exposure for one month.

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**Table S1** Copolymerization of 5-norbornene-2-yl-carboxyethyl-1-imidazole with

 5-ethylidene-2-norbornene and norbornene

Copolymer	Monomer <sup>a)</sup>	Polym. time (h)	Yield (%)	$M_{\rm n}( imes 10^4)$	$M_{\rm w}/M_{\rm n}$	Molar ratio $(x)^{b}$
PEN-im	5-ethylidene-2- norbornene	24	45	6.7	1.6	0.003
PN-im	2-norbornene	10	50	19	1.3	0.009

a) Feed molar ratio b) x in Schemen1.

Scheme S1. Proposed presence of an Fe(II)s

#### References

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