

Electronic Supplementary Information for the Manuscript:

Metal-Catalyzed Radical Polyaddition as a Novel Polymer Synthetic Route

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Experimental Section

Materials. RuCl₂(PPh)₃ (Wako), FeCl₂ (Aldrich; 99.99%), CuCl (Aldrich; 99.99%), and *n*-Bu₃P (KANTO ; > 98%) were used as received and handled in a glove-box (VAC Nexus) under a moisture- and oxygen-free argon atmosphere (O₂ < 1 ppm). PMDETA (Tokyo Kasei; > 98%) was distilled over calcium hydride before use. All other reagents were purified by usual methods.

Monomer Synthesis (1–3). Allyl 2-chloropropanoate (**1**) and 3-butenyl 2-chloropropionate (**2**) were synthesized from 2-chloropropionyl chloride (Aldrich; 97%) and the corresponding alcohols; i.e. allyl alcohol (Tokyo Kasei; > 99%) and 3-buten-1-ol (Tokyo Kasei; > 98%) for **1** and **2**, respectively. CH₂=CHCH₂C(CO₂Me)(Me)Cl (**3**) was prepared according to the literature.¹ The reaction was carried out by the syringe technique under dry argon atmosphere in an oven-dried glass tube equipped with three-

way stopcocks. A typical synthetic example for **2** is given below. 2-Chloropropionyl chloride (51.0 mL, 0.525 mol) was added dropwise with vigorous stirring to a solution of 3-buten-1-ol (42.4 mL, 0.50 mol) and triethylamine (76.7 mL, 0.55 mol) in dry THF (80.0 mL) at 0 °C. The mixture kept stirred for 1 h at 0 °C, and then over 12 h at room temperature. After the dilution with diethyl ether, the mixture was washed with 10% aqueous solution of NaHCO₃ and then water and evaporated to remove the solvents. The monomer was distilled over calcium hydride under reduced pressure to give pure 3-butenyl 2-chloropropionate (**2**) (56.0 mL, 0.354 mol) (yield = 70.9%, purity > 99%). Figure S1 shows the ¹H NMR spectra of the monomers (**1–3**).

Polymerizations. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is given below. To a suspension of FeCl₂ (50.7 mg, 0.40 mmol) in toluene (1.27 mL) was added *n*-Bu₃P (0.20 mL, 0.80 mmol), and the mixture kept stirred for 24 h at 80 °C to give a homogeneous solution of the FeCl₂(*n*-Bu₃P)_n complex. After the solution was cooled to the room temperature, 3-butenyl 2-chloropropionate (**2**) (2.53 mL, 16.0 mmol) was added. The solution was evenly charged in 8 glass tubes and the tubes were sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 100 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to -78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with toluene as an internal standard.

Measurements. Monomer conversion was determined from the concentration of

residual monomer measured by gas chromatography [Shimadzu GC-8A equipped with a thermal conductivity detector and a 3.0 mm i.d. × 2 m stainless steel column packed with SBS-200 (Shinwa Chemical Industries Ltd.) supported on Shimalite W; injection and detector temperature = 200 °C, column temperature = 160 °C] with toluene as an internal standard under He gas flow. ¹H NMR spectra were recorded in CDCl₃ at 25 °C on a Varian Gemini 2000 spectrometer, operating at 400 MHz. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-980 precision pump and a Jasco 930-RI detector. The columns were calibrated against 7 standard poly(MMA) samples (Shodex; M_p = 1990–1950000; M_w/M_n = 1.02–1.09). MALDI-TOF-MS spectra were measured on an Applied Biosystems Voyager-DE STR spectrometer (reflector mode) with dithranol (1,8,9-anthracenetriol) as the ionizing matrix and sodium trifluoroacetate as the ion source. The experiment was carried out at an accelerating potential of 22 kV, where 256 laser shots were accumulated.

References

1. J. Villiéras, D. Payan, Y. Anguelova, J.-F. Normant. *J. Organomet. Chem.*, 1972, **42**, C5.

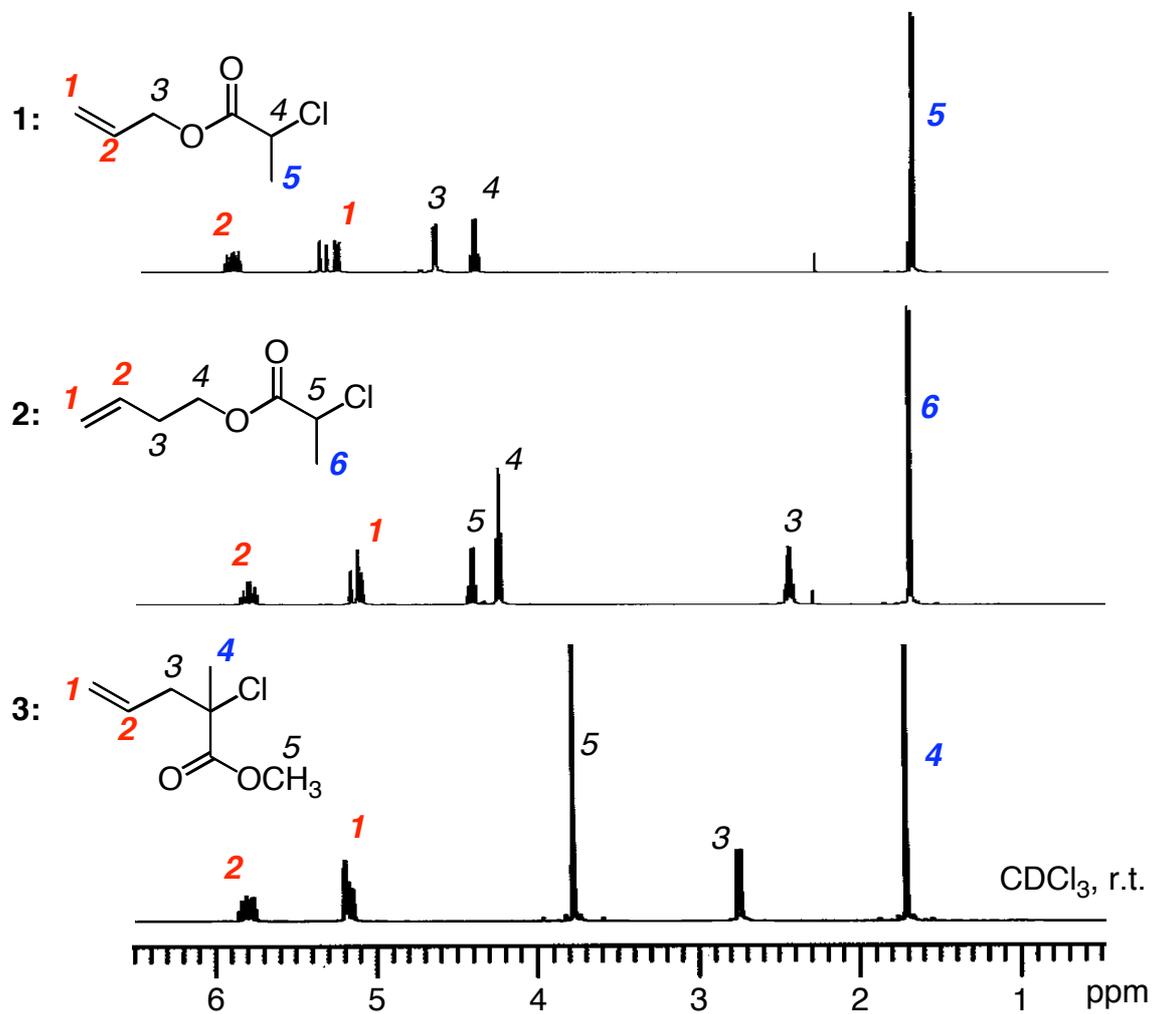


Figure S1. ^1H NMR spectra of 1–3.

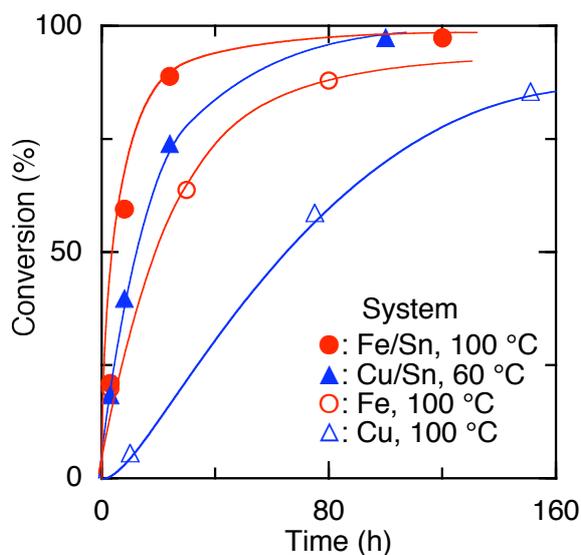


Figure S2. Effects of $\text{Sn}(\text{EH})_2$ on the polyaddition of 3-butenyl 2-chloropropionate (**2**) with the $\text{FeCl}_2/\text{Pn-Bu}_3$ or $\text{CuCl}/\text{PMDETA}$ system: $[\mathbf{2}]_0 = 4.0 \text{ M}$; $[\text{Mt}]_0 = 100 \text{ mM}$; $[\text{ligand}]_0 = 200 \text{ (Pn-Bu}_3\text{) or } 400 \text{ mM (PMDETA)}$; $[\text{Sn}(\text{EH})_2]_0 = 45 \text{ mM (EH: 2-ethylhexanoate)}$ in toluene.

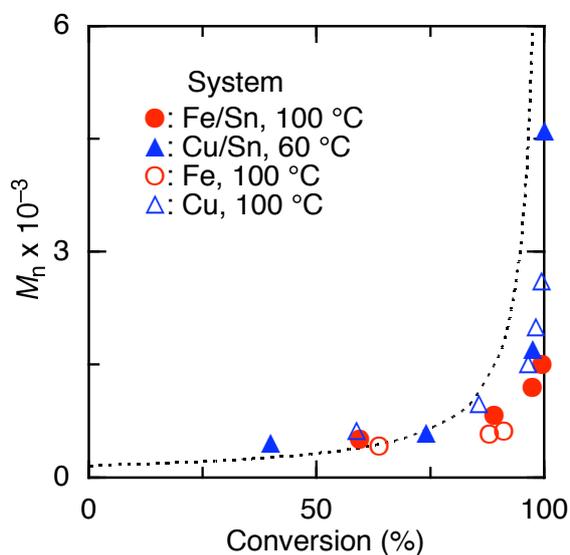


Figure S3. M_n , M_w/M_n , and MWD curves of poly(**2**) obtained in the same experiments as for Figure S2. The dotted line indicates the calculated M_n assuming the following equation: $M_n = \text{molecular weight of } \mathbf{2} / (1 - \text{conversion})$.