

Supporting Information

Heterobimetallic Block Copolymers with a Combined Main-chain/Side-chain Topology

Ye Sha^{a,*}, Zhou Zhou^a, Jiale Zhang^a, Xiaofan Chen^a, Zhenyang Luo^a, and Xiang Li^{b,*}

^aDepartment of Chemistry and Material Science, College of Science, Nanjing Forestry University, Nanjing 210037, China

^bJiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Science, Nanjing Agricultural University, Nanjing, 210095, China

1. General Information.....	2
1.1 Materials	2
1.2 Characterizations.....	2
2. Synthesis	3
2.1 Monomer synthesis	3
2.1.1 Synthesis of <i>N</i> -[3-hydroxypropyl]- <i>cis</i> -5-norbornene- <i>exo</i> -2,3-dicarboximide.....	3
2.2.2 Synthesis of M1	3
2.2.3 Synthesis of M2	4
2.2. Polymerization procedure	4
2.2.1 Synthesis of P1.....	4
2.2.2 Synthesis of P2.....	5
2.2.3 Synthesis of P3.....	5
2.2.4 Synthesis of P4.....	6
3. Characterization	6
3.1 NMR spectra of monomers and homopolymers	6
3.2 Polymerization kinetics of M1 and M2	7
3.3 Photophysical properties of homopolymers.....	7
3.4 Electrochemical properties of monomers and polymers.....	8
3.5 Magnetic test.....	9
3.6 Glass transition behavior of homopolymers	9
3.7 TEM images.....	10
3.8 NMR spectra	11
References.....	14

1. General Information

1.1 Materials

All reagents were purchased from the *Sigma-Aldrich*, *Alfa Aesar*, *J&K Chemicals*, *Energy Chemicals*, *Aladdin Reagents*, *Meryer Chemicals* or *Leyan Chemicals* and used without further purification unless otherwise stated. The polystyrene (PS) standards were purchased from Shodex Co., Ltd. Ruthenocenecarboxylic acid was prepared based on a previous work.¹ The cyclic metallocenyl alkenes, i.e., 1,1'-(2-butenyl)ferrocenedicarboxylate and 1,1'-(2-butenyl)ruthenocenedicarboxylate were prepared based on our previous works.²⁻⁵ All the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk technique unless otherwise stated. All solvents were extra dry for reactions unless otherwise stated.

1.2 Characterizations

Nuclear magnetic resonance (NMR) experiments (¹H and ¹³C) were recorded on a Bruker Avance NEO 400 instrument by using deuterated chloroform as a solvent. Chemical shifts were calibrated to the proton resonance of solvent (7.26 and 77.0 ppm for ¹H NMR and ¹³C NMR spectroscopies, respectively).

High-resolution mass spectra (HRMS) were recorded by a Waters Micromass Q-ToF mass spectrometer which utilized an ESI ionization source.

Gel permeation chromatography (GPC) curves were measured with Malvern Viscotek 270 by using THF as the mobile phase at 40 °C. The flow rate was 1 mL/min, and the injection volume was 100 µL. A refractive index detector was employed to characterize the number average molecular weight (M_n) and molecular weight distribution (\mathcal{D}) through conventional calibration by using narrow-distributed polystyrene as an internal standard.

UV-Vis absorption spectra were recorded with Shimadzu UV-2700 spectrophotometers with a 10.00 mm quartz cuvette using chloroform (10⁻⁴ mol/L) as the solvent and monochromatic light of various wavelengths over a range of 250–600 nm.

Glass transition temperature (T_g) was characterized with a Netzsch differential scanning calorimeter (DSC) calibrated with an indium standard. The heating and cooling rates were fixed at 10 °C/min from 0 °C to 200 °C.

The thermal degradation properties of the samples were probed through thermogravimetry by using a Netzsch TG 209 F1 system (Netzsch Instruments). The samples were heated from 30 °C to 800 °C at a rate of 20 K/min under nitrogen

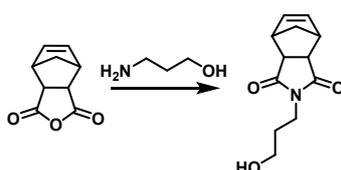
protection.

Cyclic voltammograms (CV) were recorded by a CHI600E Electrochemical Analyzer/Workstation at a scan rate of 100 mV/s in dichloromethane solution by using 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte, glassy carbon as the working electrode, platinum as the counter electrode, and a silver/silver chloride (Ag/AgCl) electrode as the standard reference electrode. All solutions were clear and transparent and thoroughly degassed before measurements.

2. Synthesis

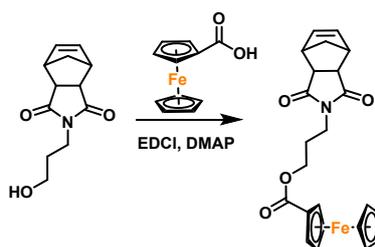
2.1 Monomer synthesis

2.1.1 Synthesis of *N*-[3-hydroxypropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide



Cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride (NDA, 1.0 g, 6.092 mmol, 1 equiv.) and 3-amino-1-propanol (0.5033 g, 0.5125 mL, 6.701 mmol, 1.1 equiv.) were dissolved in 30 mL dichloromethane (DCM), stirred, and then evaporated at 50 °C to remove all solvents. The mixture was heated to 110 °C and maintained overnight. The product was purified by silica flash chromatography (EA:PE=1:1 as eluent). The product was obtained as a colorless liquid (1.221 g, 85% yield). ¹H NMR (400 MHz, CDCl₃) δ = 6.29 (t, 2H), 3.64 (t, 2H), 3.55 (t, 2H), 3.28 (m, 2H), 2.71 (d, 2H), 2.07 (br, 1H), 1.77 (dt, 2H), 1.54 (m, 1H), 1.23 (m, 1H).

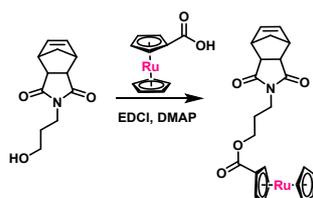
2.2.2 Synthesis of M1



N-[3-hydroxypropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide (1.221 g, 5.520 mmol, 1.1 equiv.), DMAP (0.6130 g, 5.018 mmol, 1 equiv.), and ferrocenecarboxylic acid (1.154 g, 5.018 mmol, 1 equiv.) were dissolved in 50 mL DCM. Then EDCI (1.924 g, 10.04 mmol, 2.0 equiv.) was added into the system. The reaction was stirred at room temperature overnight. The reaction mixture was washed with deionized water, saturated brine and dried over MgSO₄. The crude product was concentrated with a

rotary evaporator. The residue was purified by silica flash chromatography (EA:PE=1:2 as eluent). The product was obtained as a yellowish solid (1.815 g, 83.5% yield). ^1H NMR (400 MHz, CDCl_3) δ = 6.28 (s, 2H), 4.81 (s, 2H), 4.41 (s, 2H), 4.22 (s, 5H), 4.21 (t, 2H), 3.64 (t, 2H), 3.29 (s, 2H), 2.69 (s, 2H), 1.98 (m, 2H), 1.53 (d, 1H), 1.22 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 177.88, 171.58, 137.79, 71.29, 70.91, 70.10, 69.76, 61.38, 47.81, 45.16, 42.76, 35.75, 27.31. HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{FeNO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 456.0869, found 456.0871.

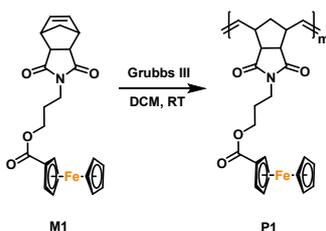
2.2.3 Synthesis of M2



N-[3-hydroxypropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide (0.3802 g, 1.718 mmol, 1.1 equiv.), DMAP (0.1908 g, 1.562 mmol, 1 equiv.), and ruthenocenecarboxylic acid (0.4300 g, 1.562 mmol, 1 equiv.) were dissolved in 20 mL DCM. Then EDCI (0.5989 g, 3.124 mmol, 2.0 equiv.) was added into the system. The reaction was stirred at room temperature overnight. The reaction mixture was washed with deionized water, saturated brine and dried over MgSO_4 . The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (EA:PE=2:3 as eluent). The product was obtained as a white solid (0.6424 g, 85.92% yield). ^1H NMR (400 MHz, CDCl_3) δ = 6.28 (s, 2H), 5.14 (s, 2H), 4.70 (s, 2H), 4.61 (s, 5H), 4.12 (t, 2H), 3.58 (t, 2H), 3.28 (s, 2H), 2.69 (s, 2H), 1.93 (m, 2H), 1.53 (d, 1H), 1.23 (d, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 177.85, 170.18, 137.80, 75.32, 72.79, 71.81, 71.60, 61.35, 47.81, 45.17, 42.75, 35.74, 27.17. HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{RuNO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 502.0563, found 502.0568.

2.2. Polymerization procedure

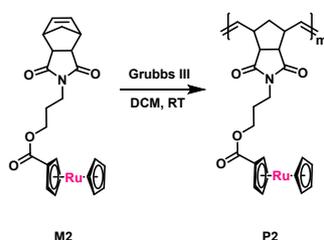
2.2.1 Synthesis of P1



M1 (100 mg, 0.2308 mmol, 40 equiv.) was dissolved in 1.2 mL anhydrous DCM. The solution was fully degassed. A solution of Grubbs III catalyst (5.104 mg, 5.770

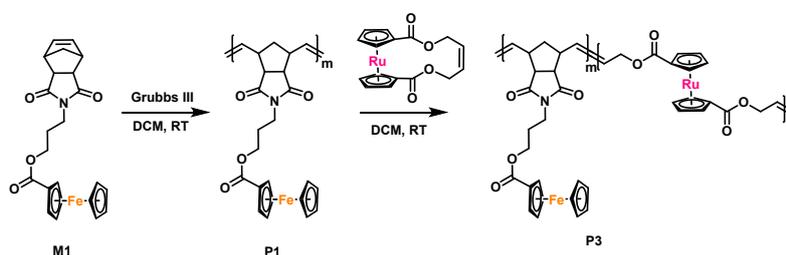
μmol , 1 equiv.) in 0.1 mL DCM was added to initiate the polymerization. The reaction was conducted at room temperature for 10 min and then quenched with several drops of EVE. The product mixture was dissolved in DCM, precipitated into methanol three times and dried, yielding 98 mg yellowish solid ($M_n = 16,900$ Da, $D = 1.08$).

2.2.2 Synthesis of P2



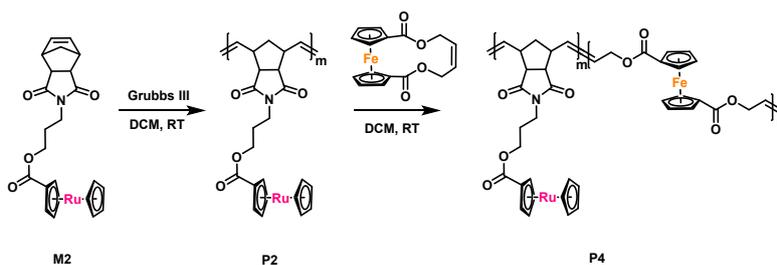
M2 (100 mg, 0.2090 mmol, 40 equiv.) was dissolved in 1.2 mL anhydrous DCM. The solution was fully degassed. A solution of Grubbs III catalyst (4.621 mg, 5.225 μmol , 1 equiv.) in 0.1 mL DCM was added to initiate the polymerization. The reaction was conducted at room temperature for 10 min and then quenched with several drops of EVE. The product mixture was dissolved in DCM, precipitated into methanol three times and dried, yielding 95 mg off-white solid ($M_n = 18,200$ Da, $D = 1.12$).

2.2.3 Synthesis of P3



M1 (100 mg, 0.2308 mmol, 40 equiv.) was dissolved in 1.2 mL anhydrous DCM. The solution was fully degassed. A solution of Grubbs III catalyst (5.104 mg, 5.770 μmol , 1 equiv.) in 0.1 mL DCM was added to initiate the polymerization. The reaction was conducted at room temperature for 10 min. Then 1,1'-(2-butenyl)ruthenocenedicarboxylate (**M3**, 0.3462 mmol, 128.6 mg, 60 eq) was added into the system. The reaction was conducted at room temperature for another 8 h and then quenched with several drops of EVE. The product mixture was dispersed in chloroform, precipitated into methanol three times and dried, yielding 180 mg yellowish solid.

2.2.4 Synthesis of P4



M2 (100 mg, 0.2090 mmol, 40 equiv.) was dissolved in 1.2 mL anhydrous DCM. The solution was fully degassed. A solution of Grubbs III catalyst (4.621 mg, 5.225 μmol , 1 equiv.) in 0.1 mL DCM was added to initiate the polymerization. The reaction was conducted at room temperature for 10 min. Then 1,1'-(2-butenyl)ferrocenedicarboxylate (**M4**, 0.4180 mmol, 136.3 mg, 80 eq) was added into the system. The reaction was conducted at room temperature for another 8 h and then quenched with several drops of EVE. The product mixture was dispersed in chloroform, precipitated into methanol three times and dried, yielding 165 mg yellowish solid.

3. Characterization

3.1 NMR spectra of monomers and homopolymers

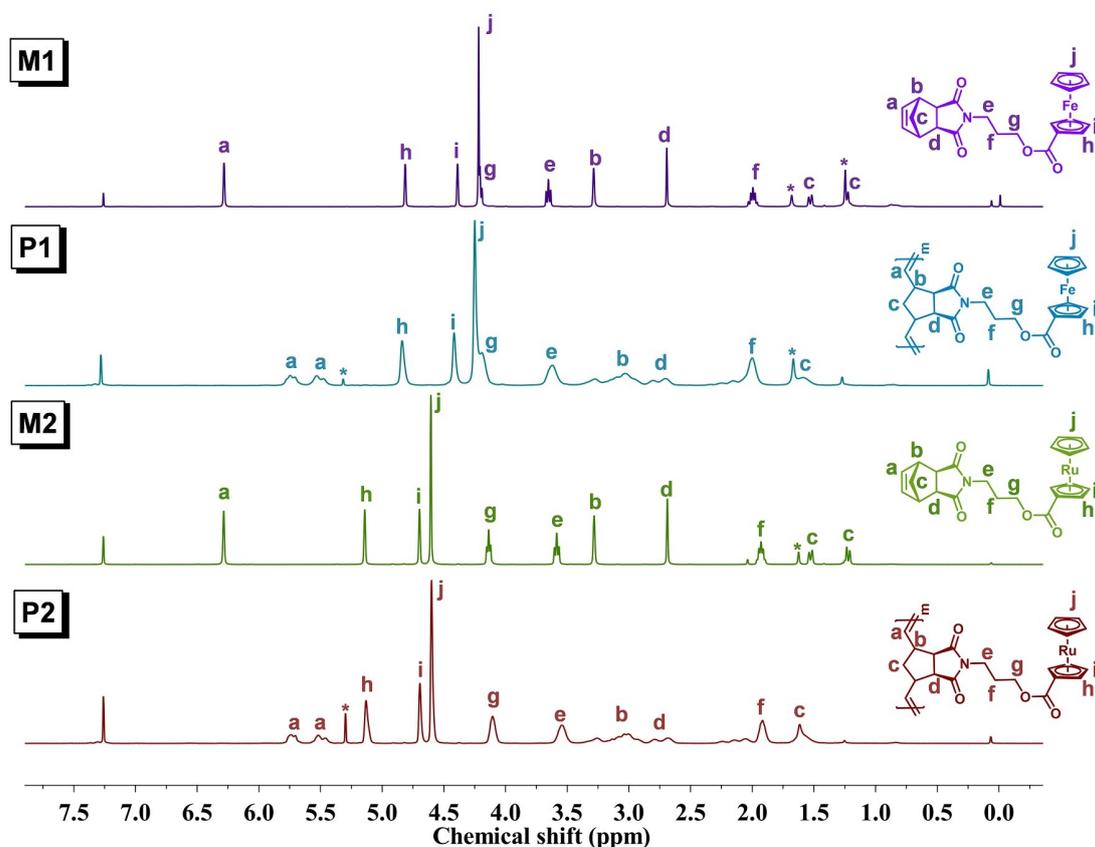


Figure S1. ^1H NMR spectra (CDCl₃) of **M1**, **M2**, **P1** and **P2**.

3.2 Polymerization kinetics of M1 and M2

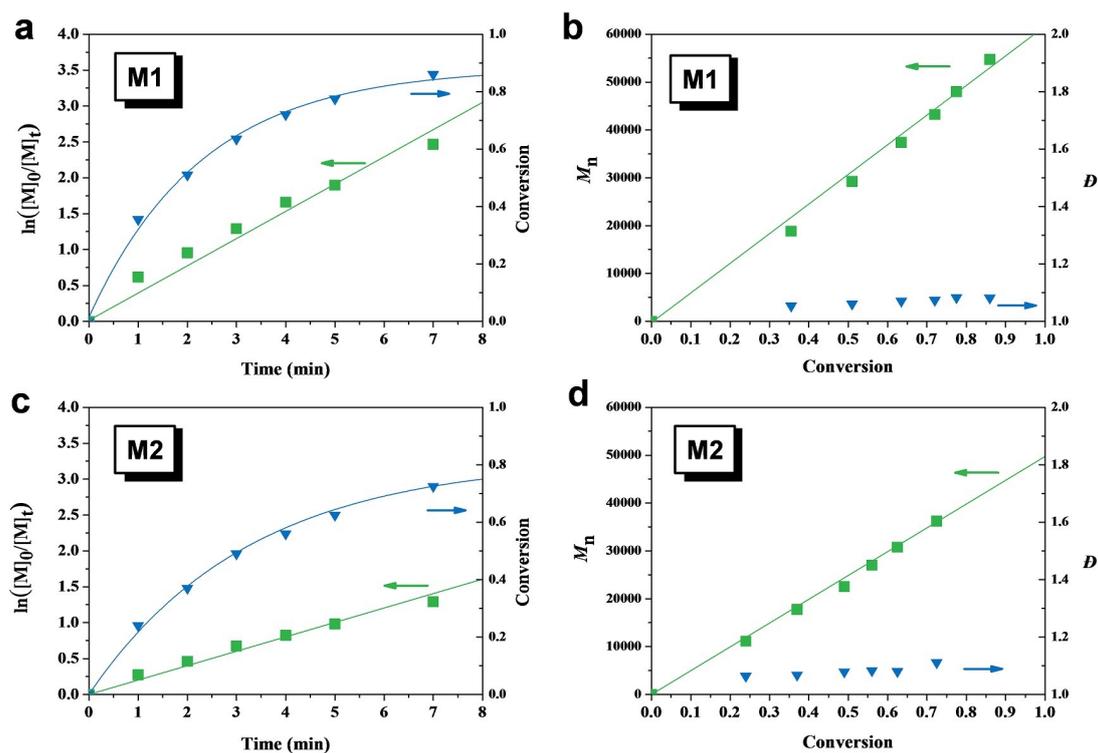


Figure S2. Polymerization kinetics of **M1**(a) (b), and **M2** (c) (d) at 0 °C ([M]:[Grubbs III]=100:1).

3.3 Photophysical properties of homopolymers

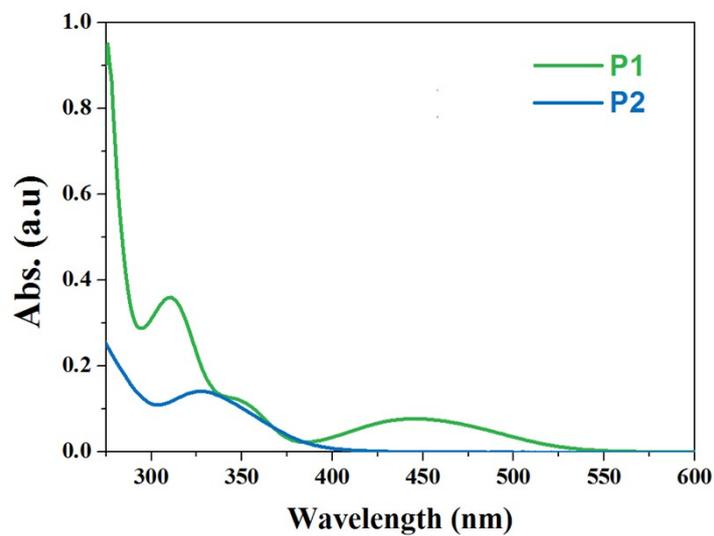


Figure S3. UV-vis spectra of **P1** and **P2** in chloroform (0.1 mg/mL).

3.4 Electrochemical properties of monomers and polymers

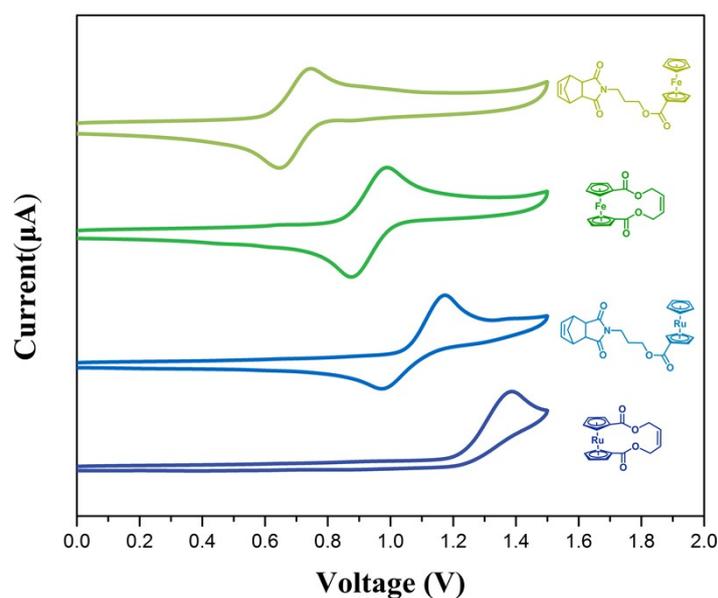


Figure S4. Compared cyclic voltammograms of four monomers in dichloromethane at a scan rate of 100 mV/s with 0.1 M TBAPF₆ as the supporting electrolyte, and Ag/AgCl as the reference electrode.

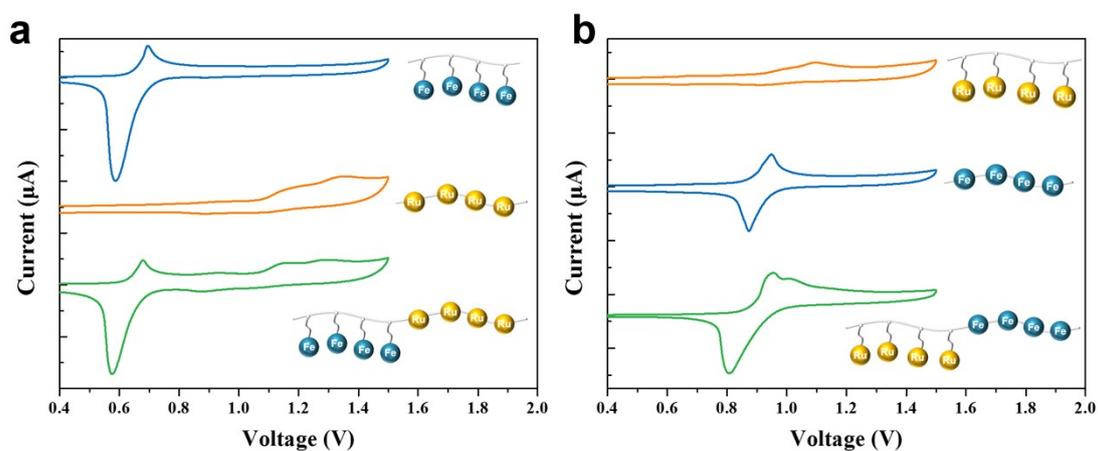


Figure S5. (a) CV of P3 and its homopolymers. (b) CV of P4 and its homopolymers. All tests were carried out in dichloromethane solution at a scan rate of 100 mV/s with 0.1 M TBAPF₆ as the supporting electrolyte, and Ag/AgCl as the reference electrode.

3.5 Magnetic test

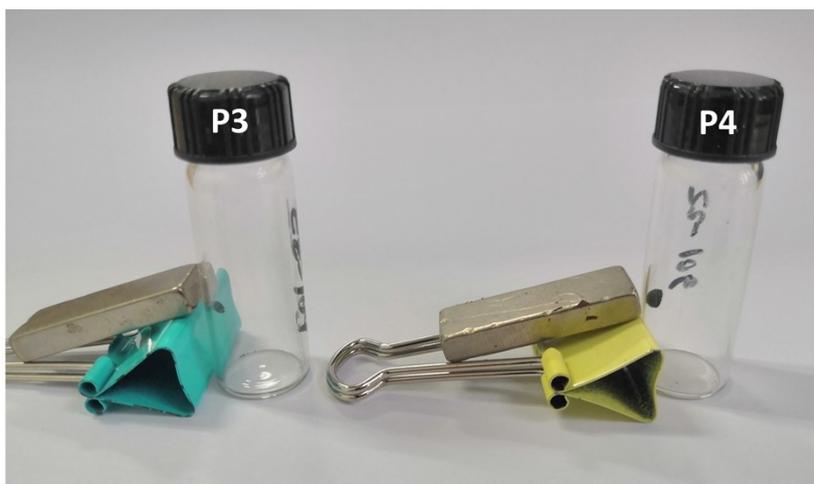


Figure S6. Magnetic test of metal alloys after pyrolysis.

3.6 Glass transition behavior of homopolymers

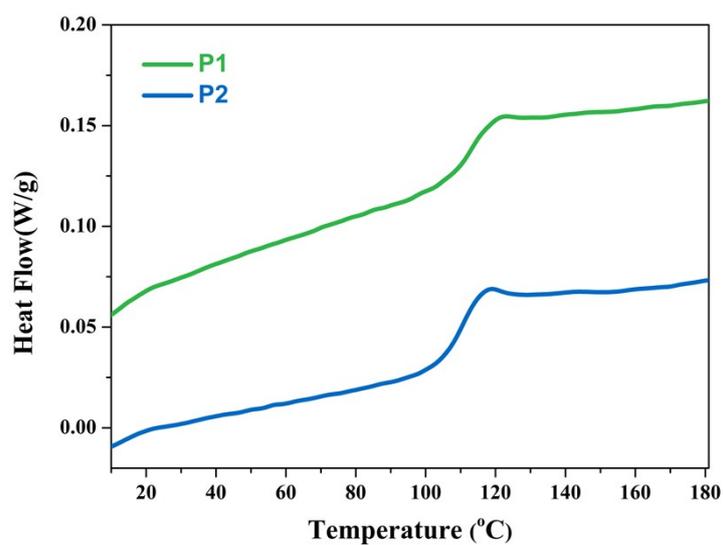


Figure S7. Second DSC heating scan (10 K/min) of homopolymers.

3.7 TEM images

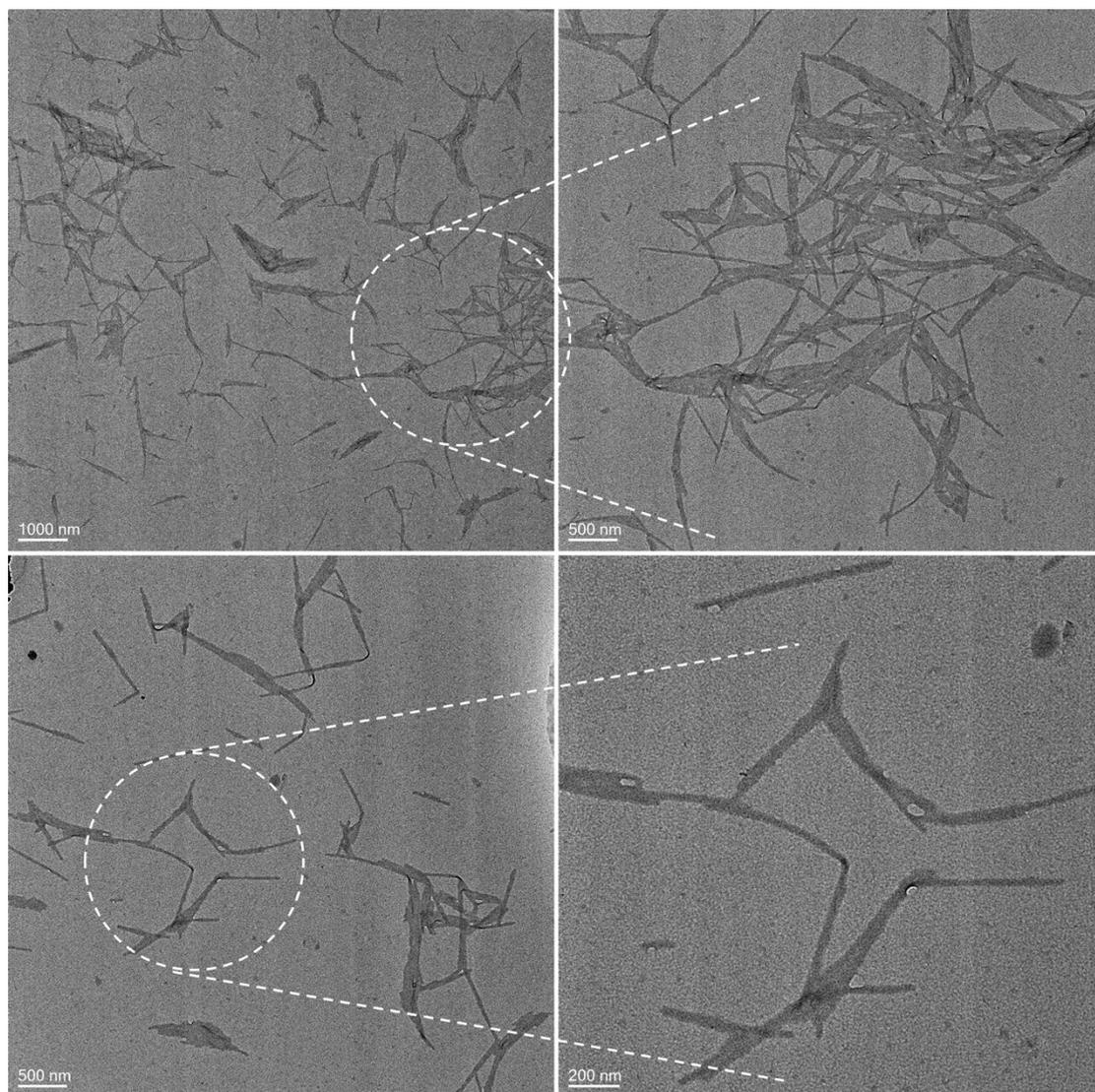


Figure S8. P3 micelles formed after polymerization.

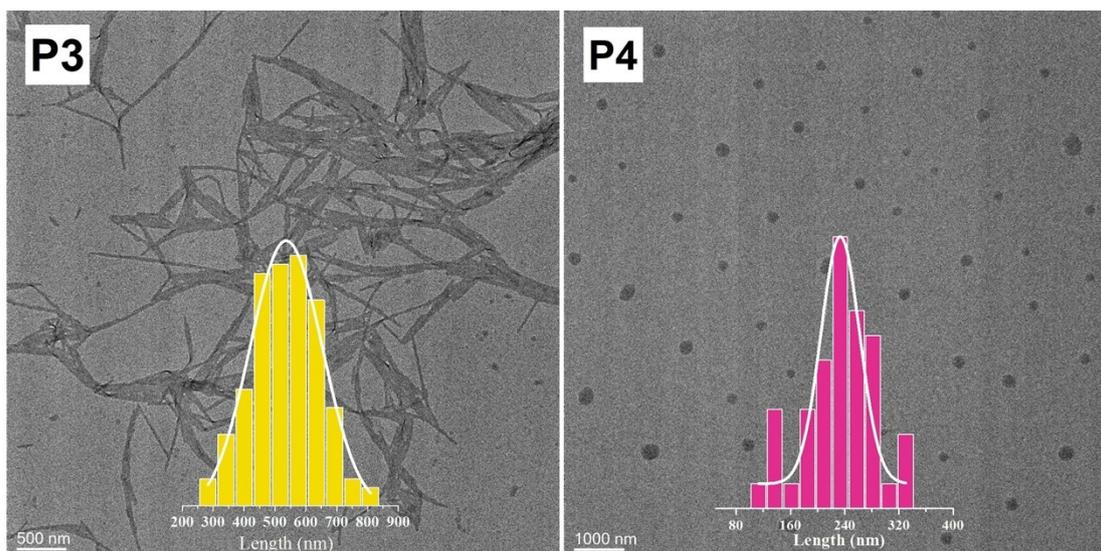


Figure S9. The statistics over the size of objects for **P3** and **P4** after polymerization.

3.8 NMR spectra

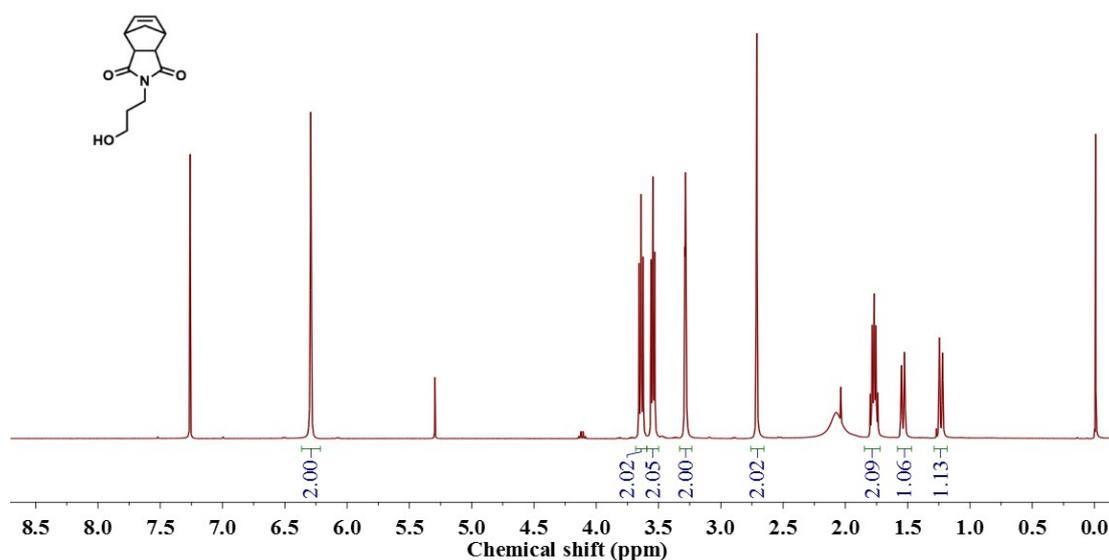


Figure S10. ^1H NMR spectrum of *N*-[3-hydroxypropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide in CDCl_3 .

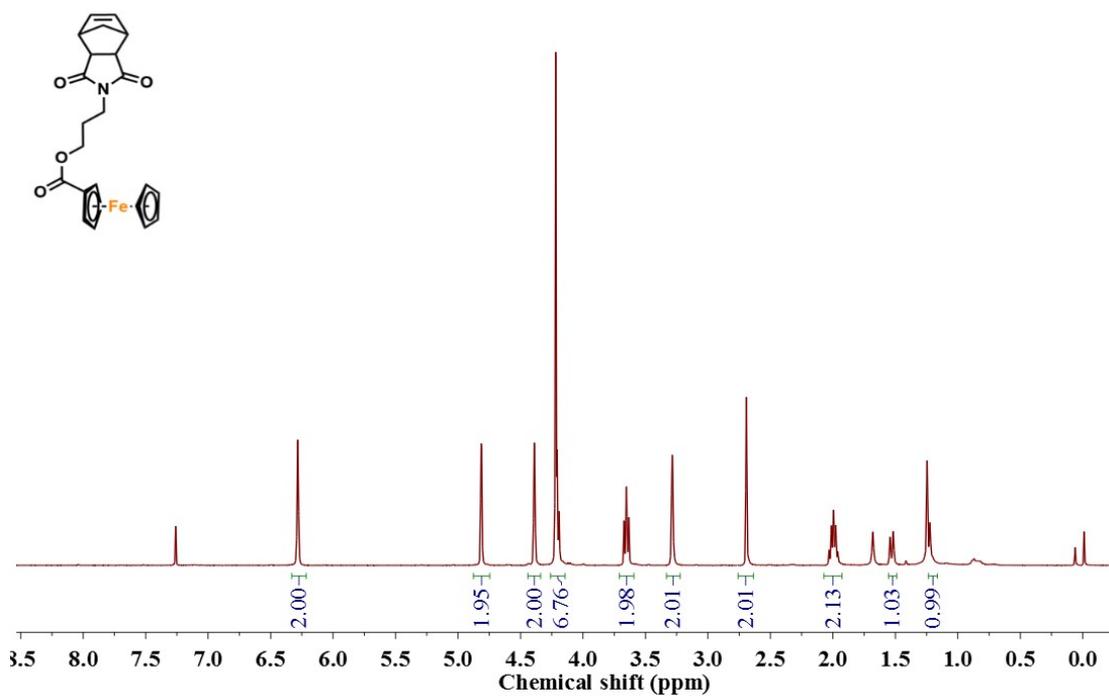


Figure S11. ¹H NMR spectrum of M1 in CDCl₃.

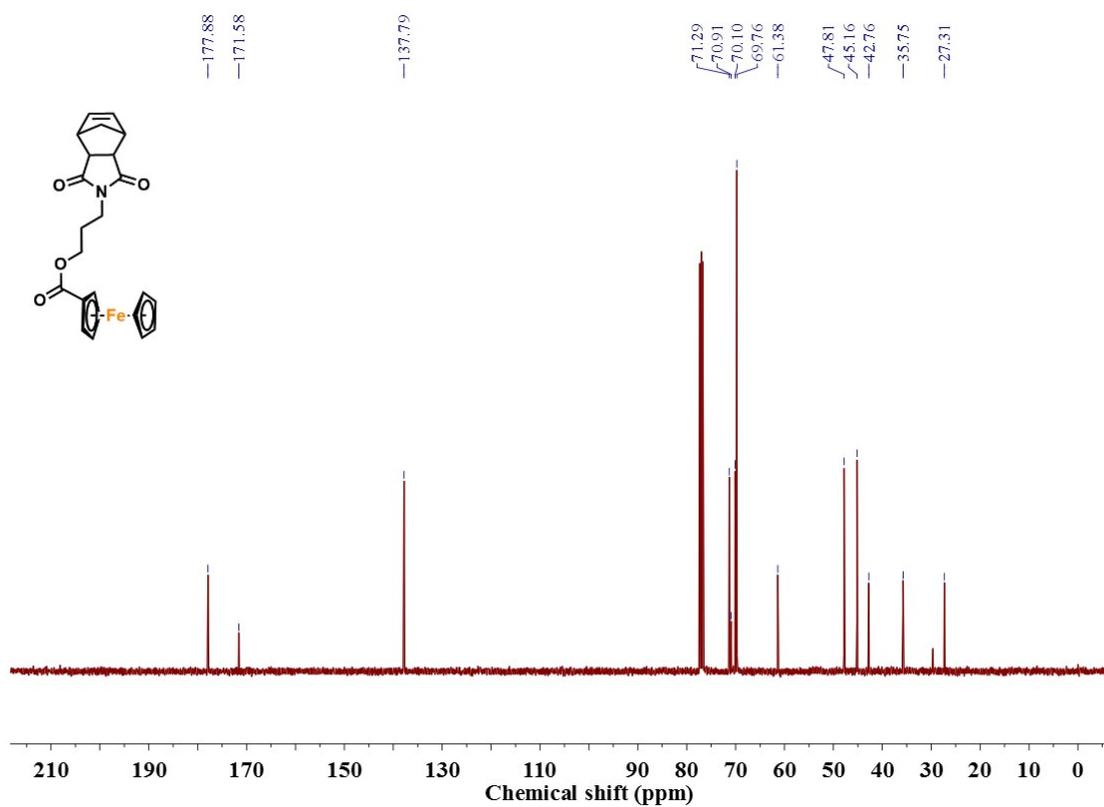


Figure S12. ¹³C NMR spectrum of M1 in CDCl₃.

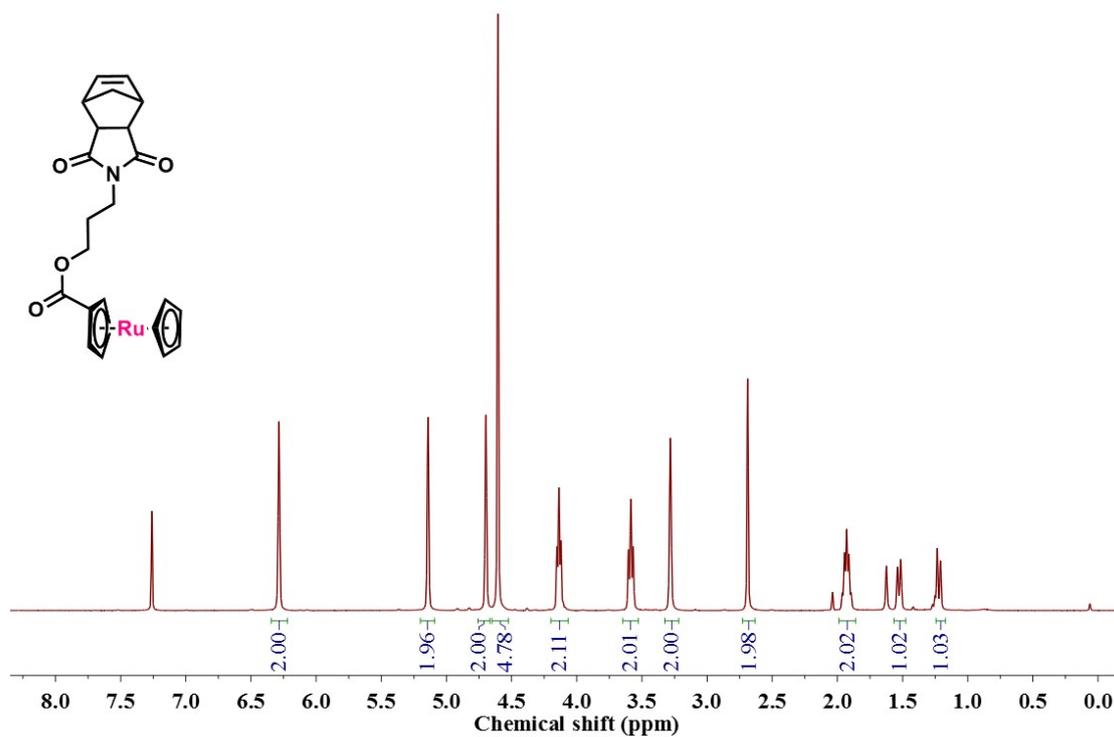


Figure S13. ^1H NMR spectrum of **M2** in CDCl_3 .

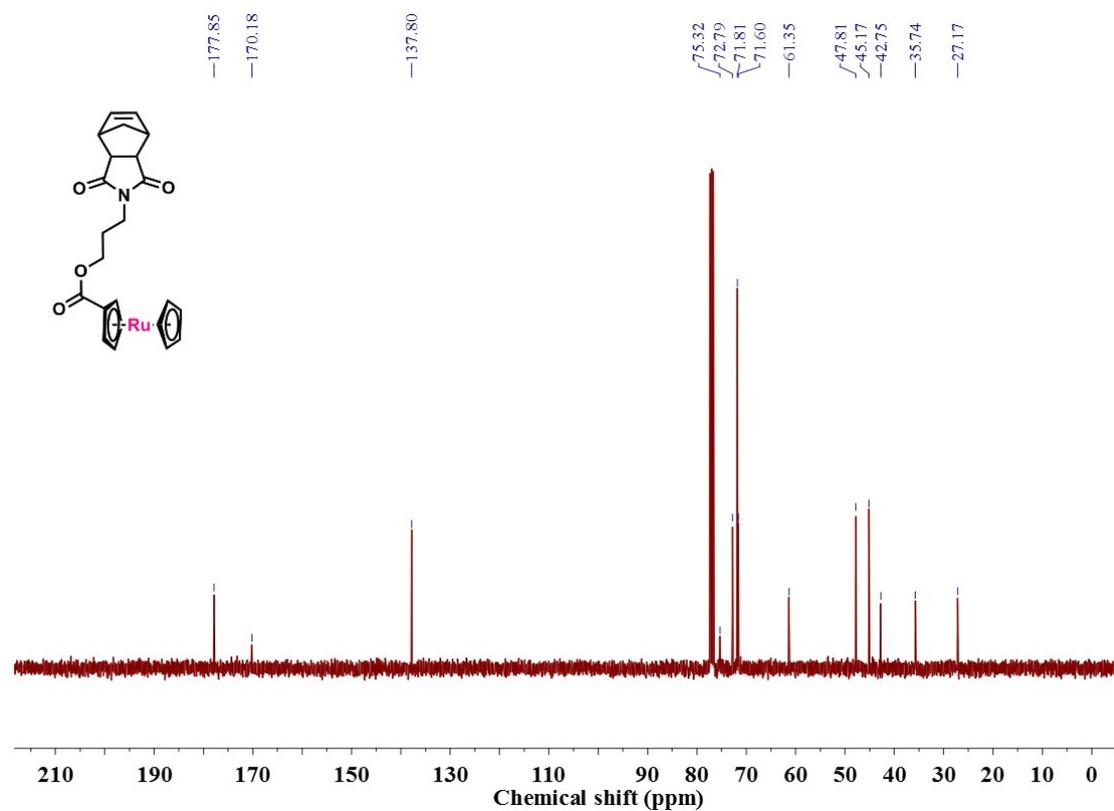


Figure S14. ^{13}C NMR spectrum of **M2** in CDCl_3 .

References

- (1) Yan, Y.; Zhang, J. Y.; Qiao, Y. L.; Ganewatta, M.; Tang, C. B. Ruthenocene-Containing Homopolymers and Block Copolymers via ATRP and RAFT Polymerization. *Macromolecules* **2013**, *46* (22), 8816-8823.
- (2) Sha, Y.; Zhang, Y.; Xu, E.; Wang, Z.; Zhu, T.; Craig, S. L.; Tang, C. Quantitative and Mechanistic Mechanochemistry in Ferrocene Dissociation. *ACS Macro Lett.* **2018**, *7* (10), 1174-1179.
- (3) Sha, Y.; Zhang, Y.; Zhu, T.; Tan, S.; Cha, Y.; Craig, S. L.; Tang, C. Ring-Closing Metathesis and Ring-Opening Metathesis Polymerization toward Main-Chain Ferrocene-Containing Polymers. *Macromolecules* **2018**, *51* (22), 9131-9139.
- (4) Sha, Y.; Zhang, Y.; Xu, E.; McAlister, C. W.; Zhu, T.; Craig, S. L.; Tang, C. Generalizing metallocene mechanochemistry to ruthenocene mechanophores. *Chem. Sci.* **2019**, *10* (19), 4959-4965.
- (5) Sha, Y.; Rahman, A.; Zhu, T.; Cha, Y.; McAlister, C.; Tang, C. ROMPI-CDSA: Ring-Opening Metathesis Polymerization Induced-Crystallization-Driven Self-Assembly of Metallo-Block Copolymers. *Chem. Sci.* **2019**, *10*, 9782-9787.