SUPPORTING INFORMATION

Bimetallic Effects for Enhanced Polar Comonomer Enchainment

Selectivity in Catalytic Ethylene Polymerization

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Scheme S1. Synthesis of ligand for bimetallic catalysts.

Scheme S2. Synthesis of ligand disodium salt.

Scheme S3. Synthesis of Ni complexes **3**, **4**, and **5**.

Polymer and Copolymer Characterization

Below are shown representative ^{13}C NMR spectra and GPC traces for the polymeric products produced in this study, as well as for physical mixtures of polyethylene and polymethylmethacrylate. In ethylene homopolymers (Figure S1), methyl branches, ethyl branches, and carbons α , β , and γ to the branch are assigned¹⁰ at 21.0, 34.8, 38.0, 27.2, and 31.5 ppm, respectively. Signals in similar regions are also observed in the ethylenecopolymer spectra of Figures S2 and S4, but with additional resonances assigned⁶⁻⁹ to the corresponding comonomer functional groups. Figure S7 shows the spectrum of a commercial PMMA sample, which serves as a comparison to the MMA/ethylene copolymer in Figure S4. Note that the observed peaks align exactly with those of a PE/PMMA copolymer and PMMA homopolymer as described in the literature¹¹. In fact, collected samples of both PE and PMMA vary so significantly in physical properties that they can be discerned by the naked eye and separated simply by extracting with dichloromethane at room temperature. Figures S3, S5, S6, S8, and S9 show representative GPC traces of these NB/PE and MMA/PE copolymers which are essentially monomodal. Additional references regarding NMR peak assignments are provided below.

Figure S1. ^{13}C NMR spectrum (100 MHz) at 130°C in $\text{C}_2\text{D}_2\text{Cl}_4$ of the polymer obtained from ethylene homopolymerization using bnuclear catalyst **FI²-Ni₂**

Figure S2. ^{13}C NMR spectrum (100 MHz) at 130°C in $\text{C}_2\text{D}_2\text{Cl}_4$ of the copolymer obtained from copolymerization of ethylene with **NB2** using catalyst **FI²-Ni₂**.

Figure S3. RI-GPC trace for the polymer produced in ethylene/ **NB2** copolymerizations using catalyst **FI²-Ni₂**.

Figure S4 ¹³C NMR spectrum (100 MHz) at room temperature in CDCl₃ of the copolymer obtained from copolymerization of ethylene with MMA using catalyst **FI²-Ni₂**. Here the 176.4, 51.0, 20.2, 45.2, and 52.9 ppm resonances correspond to carbon atoms 1- 5 respectively.

Figure S5. RI-GPC trace for the polymer produced in ethylene + MMA copolymerization using catalyst **FI²-Ni₂**. (Entry 18 in Table 1)

Figure S6. RI-GPC trace for the polymer produced in ethylene + MMA copolymerization using catalyst **FI²-Ni₂**. (Entry 18 in Table 1)

Figure S7 ^{13}C NMR spectrum (100 MHz) at room temperature in CDCl_3 of a commercial PMMA sample ($M_w = 120,000$). Here the resonances centered at 178.0, 51.8, 19.1, 44.0, and 53.4 ppm correspond to atoms 1-5 respectively.

Figure S8. RI-GPC Trace for the polymer produced in ethylene homopolymerizations in the presence of ethyl ether, using catalyst $\text{FI}^2\text{-Ni}_2$

Figure S9. RI-GPC trace for the polymer produced in ethylene homopolymerizations in the presence of acetone, using catalyst **FI²-Ni₂**.

Figure S10. RI-GPC trace of a 1:1 mixture of commercial PMMA ($M_w \sim 120,000$) and PE ($M_w \sim 70,000$). Note the significant differences in peak separation compared to that of the copolymer (Figure S6).

Figure S11. ^{13}C NMR in CDCl_3 at room temperature and GPC of the insoluble phase of the 1:1 PMMA ($M_w \sim 120,000$) and PE ($M_w \sim 70,000$) physical admixture after extracting with DCM. Note the absence of carbonyl resonances in the NMR, demonstrating that only PE remains.

Figure S12. ^{13}C NMR in CDCl_3 at room temperature and GPC of the extracted phase of the 1:1 PMMA and PE physical admixture after extracting with DCM. Note that all of the PE resonances are absent in the NMR, showing that only PMMA remains.

Figure S13. ^{13}C NMR in CDCl_3 at room temperature and GPC of the ethylene + MMA copolymer after washing with DCM. Note that the chromatogram is unchanged from those in Figures S4 and S6, illustrating that this is not a simple physical mixture of PE and PMMA, as shown in Fig S12-13.

Figure S14. ^{13}C NMR spectrum (400 MHz) at room temperature in CDCl_3 of the polymer obtained from copolymerization of ethylene with MA using catalyst $\text{FI}^2\text{-Ni}_2$.

Figure S15. RI-GPC trace for the polymer produced in ethylene + MA copolymerization using catalyst $\text{FI}^2\text{-Ni}_2$

Figure S16. COSY NMR of the polyethylene obtained from catalyst $\text{FI}^2\text{-Ni}_2$

Figure S17. COSY NMR of commercially available PMMA obtained from Aldrich

Figure S18. ^1H and ^1H COSY NMR of $\text{FI}^2\text{-Ni}_2\text{-B}$ used to determine $\text{PR}_3\text{-Ni-R}$ substituent conformation.

Figure S19. VT ^{31}P NMR spectrum of **FI²-Ni₂-B**

Figure S20. GPC with RI detection of (a) the residual insoluble PE phase and (b) the soluble PMMA phase after extracting from a physical admixture of homopolymers with hot CH_2Cl_2 .

Figure S21. Low Temperature 400MHz ^1H NMR spectra in toluene- d_8 of the monometallic **FI-Ni** butyl complex.

Figure S22. 1D-TOCSY NMR of the dibutyl **FI²-Ni₂** complex at -80 °C. Here the agostic interaction H_a is irradiated (middle) showing interaction exclusively with signals corresponding to protons 1, 2, 3, and H_b (top).

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