Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Leaching- and fragmentation-free heterogenization of late transition metal complexes as a model system to prove the mechanism of polyethylene growth

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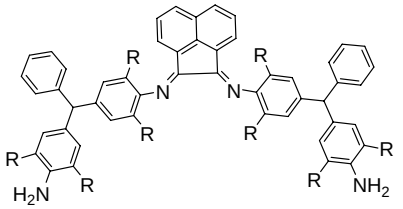
Experimental Section

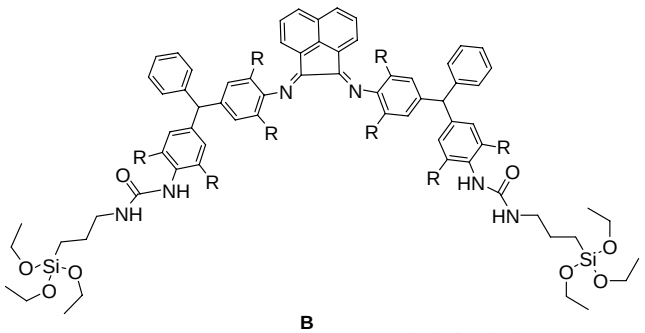
Synthesis of Ligands and Catalysts



A

R = Me (**A1**), *i*Pr (**A2**)

Recently, we reported the synthesis procedure for compound **A1** (R = Me) and **A2** (R = *i*Pr).[S1]



B

R = Me (**B1**), *i*Pr (**B2**)

General procedure: Compound B was synthesized using the reported procedure.[S2] 3-(triethoxysilyl) propylisocyanate, **L**, was added dropwise to a 20 mL THF solution of compound **A** and stirred overnight at 60 ^{o}C. After the reaction, the THF was removed under vacuum and the resulting product was purified by column chromatography [*n*-hexane/ethyl acetate (5:1.5)]. The solvent was evaporated to obtain the product and then dried at 50 ^{o}C under vacuum.

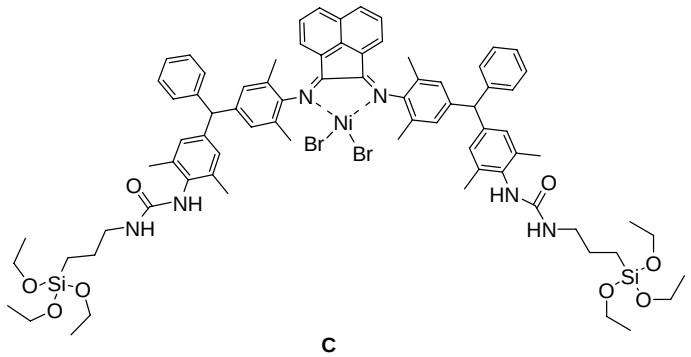
Synthesis of ligand B1 (R = Me)

Ligand **B1** was synthesized using the method reported elsewhere.[S3]

Synthesis of ligand B2 (R = *i*Pr)

Orange solid **B2** was obtained in 60% (0.46 g) yield by reacting 1.1 mmol (0.27 mL) of compound **L** with 0.5 mmol (0.52 g) of compound **A1**. δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.64 (4 H, t), 1.17 (18 H, t), 1.21 (24 H, t), 1.52 (24 H, t), 1.67 (4 H, m), 2.43 (4 H, sept.), 2.79 (4 H, sept.), 3.12(4 H, t), 3.81 (12 H, m), 5.48 (2 H, s), 5.92 (4 NH, s), 6.21 (6 H, m), 6.45 (4 H, m), 6.90 (4 H, m), 7.22 (4 H, m), 7.97 (2 H, d) 8.08 (4 H, m); δ_C (75 MHz; $CDCl_3$) δ 8.14, 17.97, 23.30, 23.81, 24.50, 27.36, 27.89, 45.35, 56.26, 59.64, 118.55, 123.38, 124.39, 126.39, 127.02, 128.55, 129.98, 130.43, 132.36, 137.11, 137.78, 138.38, 139.11, 140.59, 142.81, 144.33, 145.31, 150.92, 162.43. Found: C, 73.95; H, 8.48; N, 5.50. $C_{94}H_{128}N_6O_8Si_2$ requires C, 73.97; H, 8.45; N, 5.51%.

Synthesis of complex C.[S1]



C

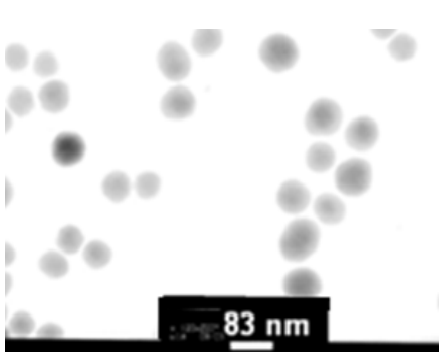
Complex **C** was synthesized using the method reported elsewhere.[S3]

Synthesis of silica gel support

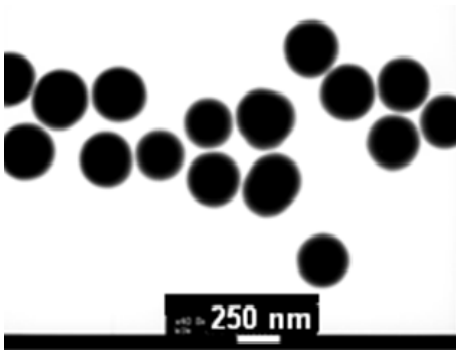
Silica gel with was synthesized using the well known Stőber method.[S4] For example, 0.5 mL TEOS (tetra ethylorthosilicate) was added to a solution of 8 mL ethanol containing 1 mL H_2O and 1 mL NH_4OH, and stirred for 3 h to form the silica gel solution, which was used directly for

immobilization. The size of the silica gel was varied by adjusting the amount of H_2O, NH_4OH and ethanol.[S4] For the nano size silica gel, the reaction mixture was stirred overnight without adding water.

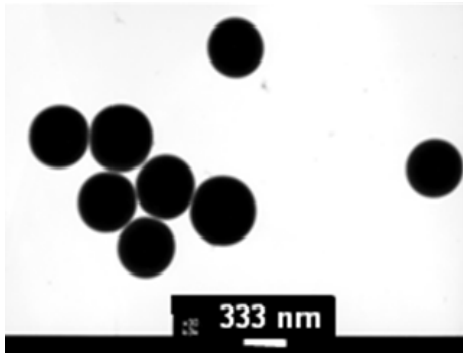
Supporting Figures



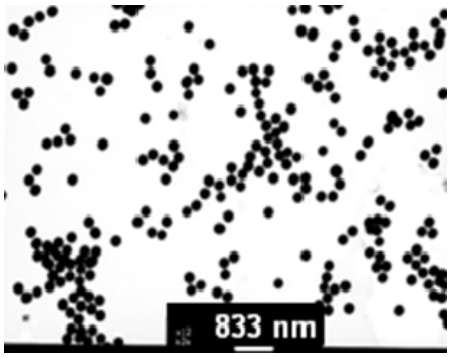
(a)



(b)



(c)



(d)

Figure S1: TEM images of silica gel having size (a) 70-90 nm; (b) 280-300 nm; (c) and (d) ~600 nm.

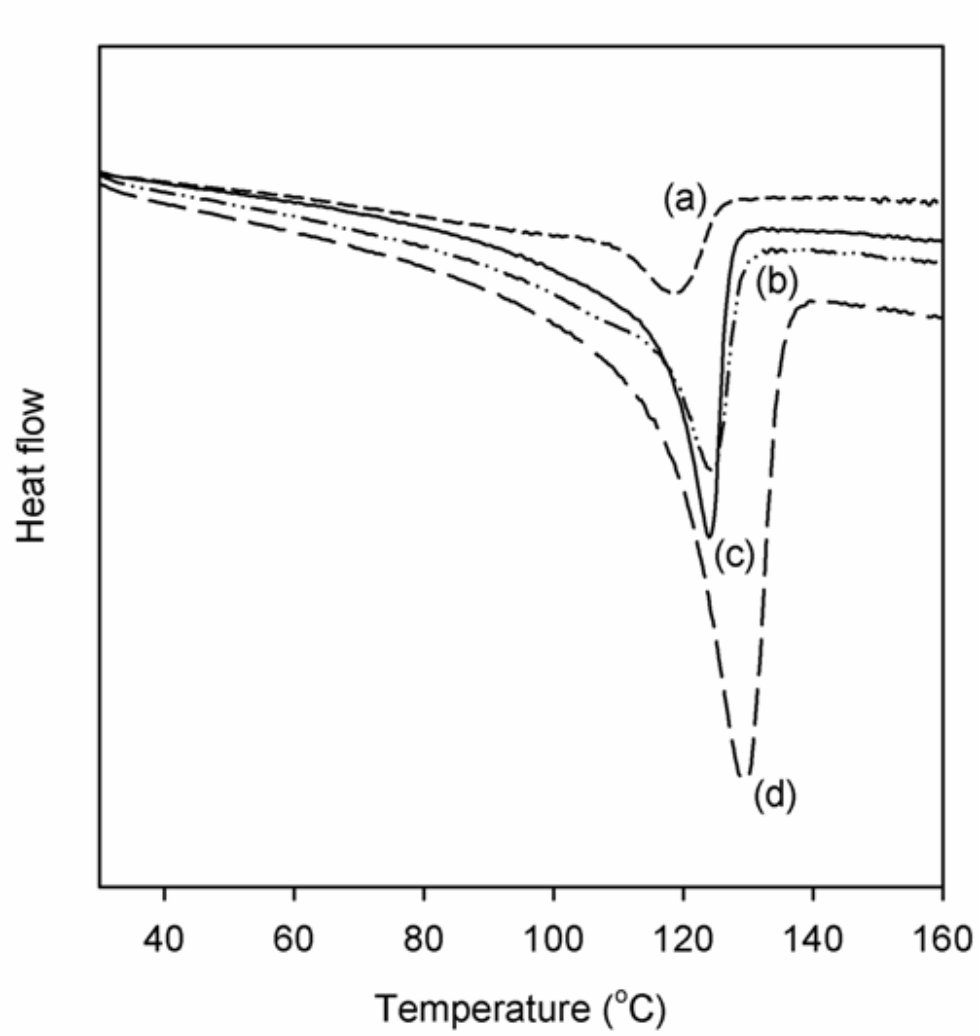


Figure S2: DSC curves of PE obtained by (a) homogeneous catalyst **C** at 5.5 bar; **(**b) catalyst **2** at 1.3 bar; (c) catalyst **2** at 5.5 bar and (d) catalyst **1a** at 5.5 bar. Polymerization condition, i) at 1.3 bar: toluene solvent = 80 mL in a 250 mL glass reactor, temperature = 30 ^{o}C, catalyst = 7 μmol for (b); ii) at 5.5 bar: toluene solvent = 40 mL in a 100 mL reactor, temperature = 30 ^{o}C, catalyst = 18 μmol for (a), (c) and (d).

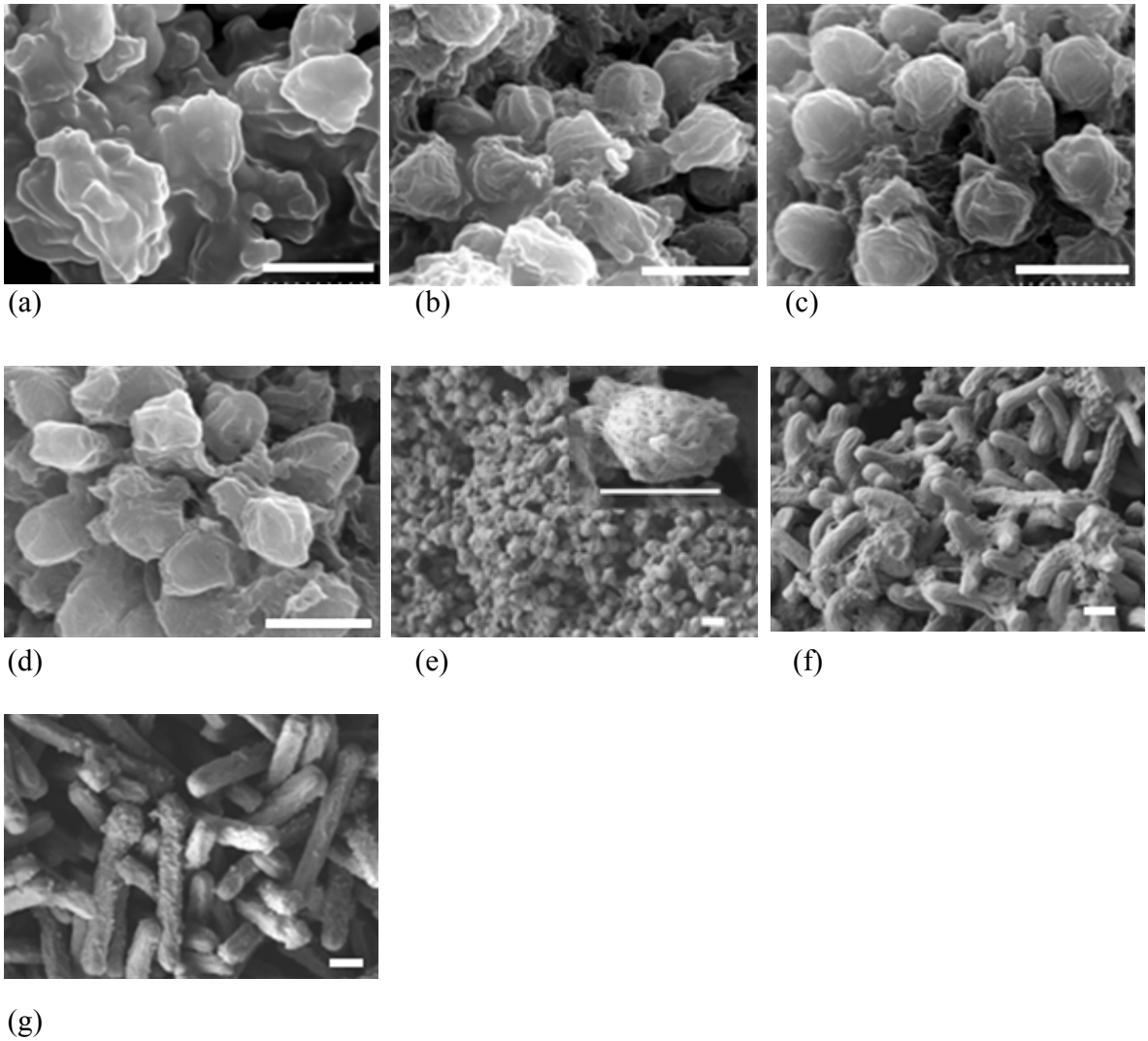


Figure S3: SEM images of PE obtained at various stage of polymerization by **1a**/EASC; (a) after 1 min; (b) after 2 min; (c) after 3 min; (d) after 4 min; (e) after 6 min; (f) after 20 min; (g) after 1 h (Scale bar = 2 μm).

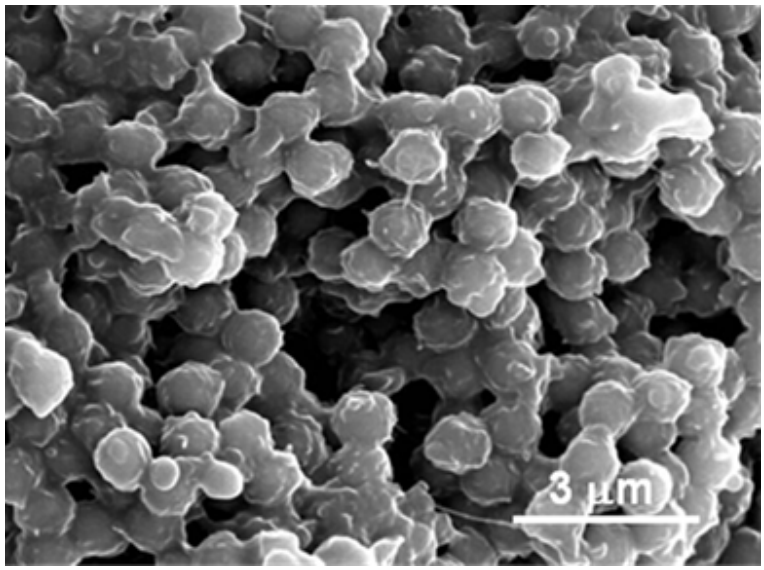


Figure S4: SEM image of PE obtained by **1a**/EASC at 70 ^{o}C in toluene.

References

S1. B. K. Bahuleyan, G. W. Son, D. W. Park, C. S. Ha and I. Kim, *J. Polym. Sci. Part. A: Polym. Chem.* 2008, **46**, 1066.

S2. (a) S. J. Lee, S. S. Lee, M. S. Lah, J. M. Houng and J. H. Jung, *Chem. Commun*. 2006, 4539. (b) J. W. Park, S. S. Park, I. Kim, and C. S. Ha, *Mol. Cryst. Liq. Cryst.* 2007, **463**, 157.

S3. B. K. Bahuleyan, B. R. Jermy, I. Y. Ahn, H. Suk, D. W. Park, C. S. Ha and I. Kim, Cat. Comm. 2009, **11**, 252.

S4. (a) W. Stőber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*1968, **26**, 62. (b) K. Lee, J. L. Look, M. T. Harris, and A. V. McCormick, *J. Colloid Interface Sci.* 1997, **194**, 78.