Supporting Information for:

B(C6F5)3 grafted inorganic fillers for supported titanium catalyzed

synthesis of UHMWPE composites

Zhengxing Bi,^a Zhao Zhang,^a Naeimeh Bahri-Laleh,^b Quan Wang,^{a,*} Chen Zou^{a,*}

Table of contents

1 General Information	2
1.1 Materials.	2
1.2 General Methods	2
1.3 Preparation of B(C ₆ F ₅) ₃ grafted inorganic supports	3
1.4 synthesis of Constrained Geometry Catalyst (CGC)	3
1.5 Preparation of Heterogeneous Catalytic System.	3
1.6 Procedure for ethylene homopolymerization.	3
1.7 Reference	4
2 Table and Figures	5
3 DSC Data of polymers	15
4 GPC Data of polymers	19

1 General Information

1.1 Materials.

All solvents were distilled after dried by sodium or purified by the PS-MD-5 (Innovative Technology) solvent purification system. Research grade ethylene was purified by dehydration column of ZHD-20 and deoxidation column of ZHD-20A. Triisobutyl aluminum (*i*Bu₃Al) was purchased from Shanghai Macklin Biochemical Co., Ltd. Powders of SiO₂ (~20 nm), TiO₂ (20-40 nm), Al₂O₃ (10-15 nm), ZnO (30-80 nm), MgO (~20 nm) were obtained from Nanjing XFNANO Materials Tech Co., Ltd., China. These Powders were treated in a tube furnace at 600 °C for 6 h before use.

1.2 General Methods.

All manipulations of water- and air-sensitive compounds were carried out using standard Schlenk techniques or glovebox under a nitrogen atmosphere. The MAS NMR experiments were performed on a 400 MHz WB Solid-State Nuclear Magnetic Resonance Spectrometer. Deuterated solvents used for Liquid NMR spectroscopy were dried and distilled prior to use. Liquid NMR spectra were recorded on a Superconducting Fourier Nuclear Magnetic Resonance Spectrometer at ambient temperature. Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 160 °C using 1,2,4-trichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm³/g and R = 0.67 for polystyrene and $K = 5.90 \times 10-2$ cm3/g and R = 0.69 for polyethylene. Differential scanning calorimetry (DSC) analyses were performed on a TA differential scanning calorimeter Q2000, and the DSC curves of the samples were recorded under a nitrogen atmosphere at a heating rate of 10 °C/min from 40 to 150 °C, cooled to 40 °C at 10 °C/min, and then heated to 150 °C at 10 °C/min marked as cycle 3 for analyze. SEM images were obtained by Cold Field Emission Scanning Electron Microscope (SU8220). Inductive coupled plasma (ICP) emission spectrometer analyses (Prodigy ICP, Leeman Laboratories, USA) were carried out with wavelength range of 165–800 nm and resolution ≤ 0.005 nm. Stress/strain experiments were performed at room temperature at 10 mm/min using a UTM2502

universal tester. At least two specimens of each polymer were tested. The test specimens had the following dimensions: gauge length, 28 mm; width, 2 mm; and thickness, 1 mm. The decomposition of polymer films was investigated by exposing the samples to UV light under a UV exposure unit (300-400 nm, Irradiance=50 w/m², Test chamber temperature=35 °C). Thermal diffusivity was measured by Laser Thermal Instrument (Netzsch LFA467) at 30 °C.

1.3 Preparation of B(C₆F₅)₃ grafted inorganic supports.

lg inorganic supports (SiO₂, Al₂O₃, TiO₂, MgO and ZnO) and B(C₆F₅) (323.3 mg, 0.600 mmol) were loaded into a Schlenk tube under argon. Dry toluene (15 mL) was vapor-transferred into the reactor, and the slurry was stirred under N₂ for 72 h at 100°C. The solvent was removed under a vacuum and the solid was wash three times with toluene and stored under N₂ at room temperature.

1.4 synthesis of Constrained Geometry Catalyst (CGC).

Constrained Geometry Catalyst (CGC) was synthesized by following the literatures procedures.¹

1.5 Preparation of Heterogeneous Catalytic System.

SiO₂-B-CGC, Al₂O₃-B-CGC, TiO₂-B-CGC, MgO-B-CGC, ZnO-B-CGC were all prepared according to the follow method. The B(C₆F₅)₃ grafted inorganic supports (1.0 g) was dispersed in toluene. The catalyst (50 μ mol) toluene solution was added dropwise and stirred for 6 hours. The solid was collected and rinsed with toluene until there was no catalyst in the filtrate, dried under vacuum and re-suspended in toluene for polymerization. The maximum adsorption capacity of CGC on SiO₂-B, Al₂O₃-B, TiO₂-B, MgO-B, ZnO-B was determined to be 10.63 μ mol cat. /1 g SiO₂-B, 6.17 μ mol cat. /1 g Al₂O₃-B, 8.85 μ mol cat. /1 g TiO₂-B, 8.06 μ mol cat. /1 g MgO-B, 9.66 μ mol cat. / 1 g ZnO-B.

SiO₂-Al-CGC, Al₂O₃-Al-CGC and MgO-Al-CGC were all prepared according to the follow method. The inorganic supports (1.0 g) was dispersed in toluene and 5mL AlⁱBu₃(1M in toluene) were added to stirred for 12 hours. The solid was collected and rinsed with toluene until the extra AlⁱBu₃ was removed. The obtained solid was dispersed in toluene again, CGC-Ti (50 µmol) toluene solution was added dropwise and stirred for 6 hours. The solid was collected and re-suspended in toluene

for polymerization.

1.6 Procedure for ethylene homopolymerization.

All homopolymerization reactions were performed in a 200 mL Quick-open Micro Autoclaves/Pressure Vessels purchased from Anhui Kemi Machinery Technology Co., Ltd. The reactor was cleaned and evacuated at 120 °C for at least an hour and was refilled with nitrogen at least three times before polymerization. The certain amounts of toluene were added into the reactor under a nitrogen atmosphere, and the mixture was stirred continuously. When the temperature was established, the *i*Bu₃Al and catalyst solution of toluene or the heterogeneous catalytic system were added into the reactor. The reactor was then pressurized with ethylene. The polymerization was conducted for the certain time and terminated with acidic alcohol. The polymers obtained were washed by alcohol to remove *i*Bu₃Al and ligand residue and dried under vacuum at 80 °C for 6 h until a constant weight was reached.

1.7 Reference

1 L. Resconi, I. Camurati, C. Grandini, M. Rinaldi, N. Mascellani and O. Traverso, *Journal of Organometallic Chemistry*, 2002, **664**, 5–26.

2 Table and Figures



Figure S1. Solution-state ¹⁹F NMR spectra of supernatant after three days of the reaction of MgO with $B(C_6F_5)_3$. (Toluene-d₈)



Figure S2. SEM-EDS mapping results of $B(C_6F_5)_3$ grafted MgO. (a) SEM image. (b) SEM-EDS mapping results. (c) O element mapping. (d) Mg element mapping. (e) B element mapping. (f) F element mapping.



Figure S3. SEM-EDS mapping results of $B(C_6F_5)_3$ grafted Al_2O_3 . (a) SEM image. (b) SEM-EDS mapping results. (c) O element mapping. (d) Al element mapping. (e) B element mapping. (f) F element mapping.



Figure S4. SEM-EDS mapping results of $B(C_6F_5)_3$ grafted TiO₂. (a) SEM image. (b) SEM-EDS mapping results. (c) O element mapping. (d) Ti element mapping. (e) B element mapping. (f) F element mapping.



Figure S5. Solution-state $^{19}\rm F$ NMR spectra of supernatant after three days of the reaction of SiO_2 with B(C_6F_5)_3. (Toluene-d_8)



Figure S6. Solution-state ¹⁹F NMR spectra of supernatant after three days of the reaction of TiO_2 with $B(C_6F_5)_3$. (Toluene-d₈)



Figure S7. Solid-state ¹⁹F NMR spectra of $B(C_6F_5)_3$ grafted SiO₂.



Figure S8. Solid-state ¹⁹F NMR spectra of SiO₂-B-CGC.



Figure S9. Polymer morphology. (a) Photos of the polyethylene composites from MgO-B-CGC in reactor at 80°C. (b) Photos of the polyethylene composites from MgO-B-CGC at 80°C. (c) and (d) SEM images the polyethylene composites from MgO-B-CGC at 80°C.



Figure S10. Polymer morphology. (a) Photos of the polyethylene composites from Al_2O_3 -B-CGC in reactor at 80°C. (b) Photos of the polyethylene composites from Al_2O_3 -B-CGC at 80°C. (c) and (d) SEM images the polyethylene composites from Al_2O_3 -B-CGC at 80°C.



Figure S11. Stress-strain curves of samples obtained using CGC at 80°C.



Figure S12. Stress-strain curves of samples obtained using SiO₂-B-CGC at 80°C.



Figure S13. Stress-strain curves of samples obtained using TiO₂-B-CGC at 80°C.



Figure S14. Stress-strain curves of samples obtained using Al₂O₃-B-CGC at 80°C.



Figure S15. Stress-strain curves of samples obtained using MgO-B-CGC at 80°C.



Figure S16. WCA of polyethylene obtained using CGC at 80°C. (Average 102.4°)



Figure S17. WCA of polyethylene obtained using SiO₂-B-CGC at 80°C. (Average 82.9°)



Figure S18. WCA of polyethylene obtained using Al₂O₃-B-CGC at 80°C. (Average 79.9°)



Figure S19. WCA of polyethylene obtained using TiO₂-B-CGC at 80°C. (Average 86.4°)



Figure S20. WCA of polyethylene obtained using MgO-B-CGC at 80°C. (Average 90.0°)

Ent.	Cat.	UV time(h)	Mn
1	TiO ₂ -B-CGC	0	203.5
2	TiO ₂ -B-CGC	13	63.1
3	TiO ₂ -B-CGC	32	18.1
4	TiO ₂ -B-CGC	47	7.0
5	TiO ₂ -B-CGC	57	4.0
6	CGC	0	45.2
7	CGC	13	44.6
8	CGC	47	43.3
9	CGC	57	42.2

Table S1. Molecular weight of polyethylene nanocomposite obtained using TiO2-B-CGC after UV irradiation for different time.



Figure S21. Curves of stress and strain of polyethylene nanocomposite obtained using TiO2-B-CGC after 47 hours UV irradiation



Figure S22. Curves of stress and strain of polyethylene nanocomposite obtained using TiO2-B-CGC after 57 hours UV irradiation

3 DSC Data of polymers



Figure S23. DSC of the polymer sample from Table 1, Entry 1.



Figure S24. DSC of the polymer sample from Table 1, Entry 2.



Figure S25. DSC of the polymer sample from Table 1, Entry 3.



Figure S26. DSC of the polymer sample from Table 1, Entry 4.



Figure S27. DSC of the polymer sample from Table 1, Entry 5.



Figure S28. DSC of the polymer sample from Table 1, Entry 6.



Figure S29. DSC of the polymer sample from Table 1, Entry 7.



Figure S30. DSC of the polymer sample from Table 1, Entry 8.



Figure S31. DSC of the polymer sample from Table 1, Entry 9.



Figure S32. DSC of the polymer sample from Table 1, Entry 10.



Figure S33. DSC of the polymer sample from Table 1, Entry 11.



Figure S34. DSC of the polymer sample from Table 1, Entry 12.



Figure S35. DSC of the polymer sample from Table 1, Entry 13.



Figure S36. DSC of the polymer sample from Table 1, Entry 14.



Figure S37. DSC of the polymer sample from Table 1, Entry 15.

4 GPC Data of polymers



Figure S38. GPC of the polymer sample from Table 1, Entry 1.



Figure S39. GPC of the polymer sample from Table 1, Entry 2.



Figure S40. GPC of the polymer sample from Table 1, Entry 3.



Figure S41. GPC of the polymer sample from Table 1, Entry 4.



Figure S42. GPC of the polymer sample from Table 1, Entry 5.



Figure S43. GPC of the polymer sample from Table 1, Entry 6.



Figure S44. GPC of the polymer sample from Table 1, Entry 7.



Figure S45. GPC of the polymer sample from Table 1, Entry 8.



Figure S46. GPC of the polymer sample from Table 1, Entry 9.



Figure S47. GPC of the polymer sample from Table 1, Entry 10.



Figure S48. GPC of the polymer sample from Table 1, Entry 11.



Figure S49. GPC of the polymer sample from Table 1, Entry 12.



Figure S50. GPC of the polymer sample from Table 1, Entry 13.



Figure S51. GPC of the polymer sample from Table 1, Entry 14.



Figure S52. GPC of the polymer sample from Table 1, Entry 15.



Figure S53. GPC of the polymer sample from Table S1, Entry 2.



Figure S54. GPC of the polymer sample from Table S1, Entry 3.



Figure S55. GPC of the polymer sample from Table S1, Entry 4.



Figure S56. GPC of the polymer sample from Table S1, Entry 5.



Figure S57. GPC of the polymer sample from Table S1, Entry 7.



Figure S58. GPC of the polymer sample from Table S1, Entry 8.



Figure S59. GPC of the polymer sample from Table S1, Entry 9.