Supporting Information For:

High activity acetylene polymerisation with a bis(imino)pyridine iron(II) catalyst

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General Details

Unless noted otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk techniques, or in a nitrogen glovebox. Solvents were purified by passage through an Innovative Technologies solvent purification system and, where appropriate, stored over a sodium mirror. Acetylene (99.0%) was purified by passage through a column of activated molecular sieves (3Å) and alumina. GC analysis showed that no acetone was present in the purified acetylene. The precatalyst, 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride, was prepared according to literature procedures.[1] Methylaluminoxane (MAO), 10 wt% in toluene, was supplied by Albemarle.

IR spectroscopy, ICP-MS and SEM were performed by the Central Science Laboratory at the University of Tasmania. IR spectra were recorded on a Bruker Vertex 70 unit with a ZnSe Single Reflection ATR crystal, with an Extended ATR correction applied. SEM was performed using an FEI Quanto 600 scanning electron microscope with an EDAX Sapphier ultra-thin window energy dispersive x-ray spectrometer. ICP-MS was performed on an ELEMENT High-Resolution ICP-MS operation at medium resolution mode (3000 $m/\Delta m$).

Acetylene Polymerisation

In a typical run, polymerisation was conducted in a 400 mL Lab-Crest glass pressure reactor. The oven dried reaction vessel was purged with argon for 30 minutes followed by acetylene. Solvent (toluene) was then introduced such that a final volume of 50 mL would be obtained. The Fe catalyst **1** was dissolved/suspended in toluene in a Schlenk flask under argon, and activated with 100 equivalents of MAO. An aliquot (5 µmol of Fe) of the activated catalyst was then added to the reactor before pressurising to 1 bar gauge with acetylene, with rapid stirring. External cooling was applied early in the run to maintain the temperature at 20-23 °C. After the desired run time, acetylene was bled and the gel collected and washed with toluene. Evaporation of the solvent afforded dry polyacetylene, which was weighed to determine the yield.

Polyacetylene Film Formation

Polyacetylene films were formed in Schlenk flasks under a pressure of acetylene of 1 bar gauge. The Fe catalyst **1** was activated with 100 equivalents of MAO in a separate flask. An aliquot of the activated catalyst was added to toluene (10-50 mL) such that the desired catalyst concentration was obtained. Thereafter the flask was briefly evacuated to remove argon, before acetylene was admitted. The formation of a surface layer of polyacetylene occurs instantly. After 10 minutes the flask was purged with argon and the toluene removed with a syringe. The remaining film was washed twice with toluene, such that the washings were colorless, and then dried under vacuum at room temperature. Shiny silver-gold films resulted. In this work, the formation of films was carried out successfully at Fe concentrations ranging from 100 µM to 4 µM. The IR spectrum of a film formed at [Fe] = 20 µM is shown in Figure S1 below.

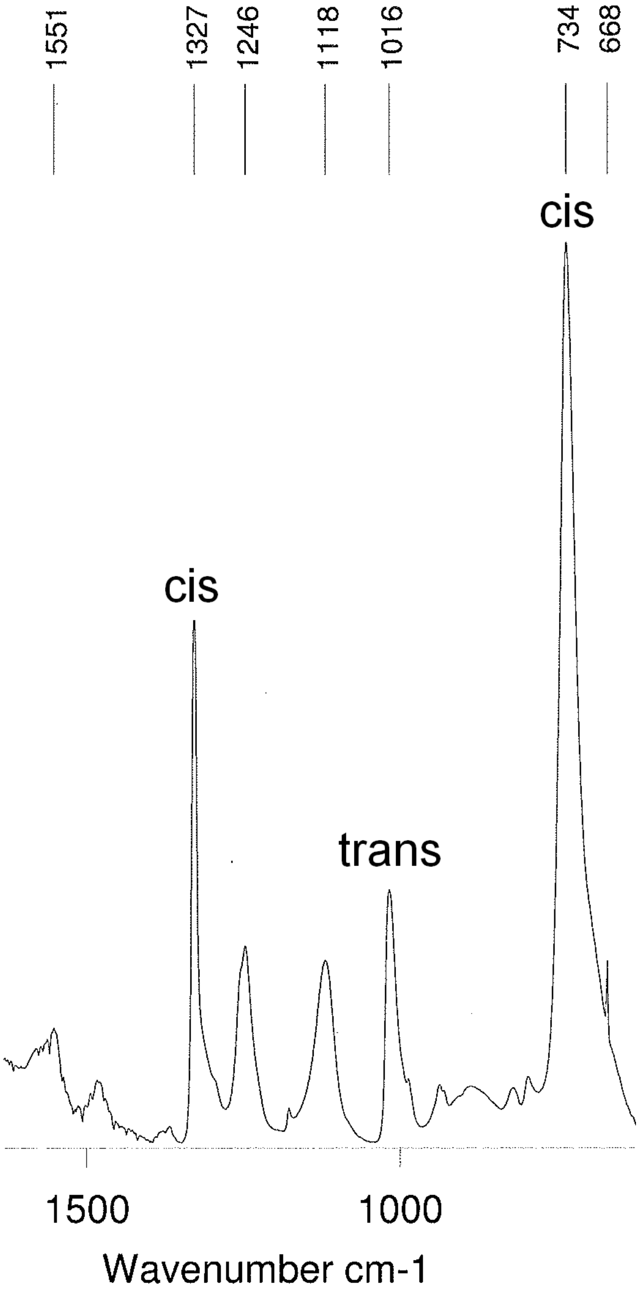

Figure S1. IR spectrum (C-H deformation region) of a polyacetylene film formed by **1**/MAO in toluene.

Fe Content of Polyacetylene by ICP-MS

Polyacetylene was prepared in a pre-weighed Schlenk flask as described above, and the toluene solvent decanted from the polymer. The flask was placed in a furnace along with an empty flask (blank), and the temperature ramped at 300 °C/h to 500 °C, held for 2 hours, and then cooled to room temperature. To each flask was added 1mL of concentrated HNO_3 and 2 mL of concentrated HCl. After stirring at 100 °C for 2 hours, Milli-Q water was added to each flask so that the total content of each was 25 g. The samples were diluted 1:100 before ICP-MS analysis. The final iron concentration (12.1 ppm) was obtained after subtracting the blank background, and compared to the maximum possible concentration given the quantity of catalyst **1** added (13.2 ppm).

Reference

1 G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, and D. J. Williams, *Chem. Commun.*, 1998, 849.