A well-defined metallocene catalyst supported on polystyrene beads

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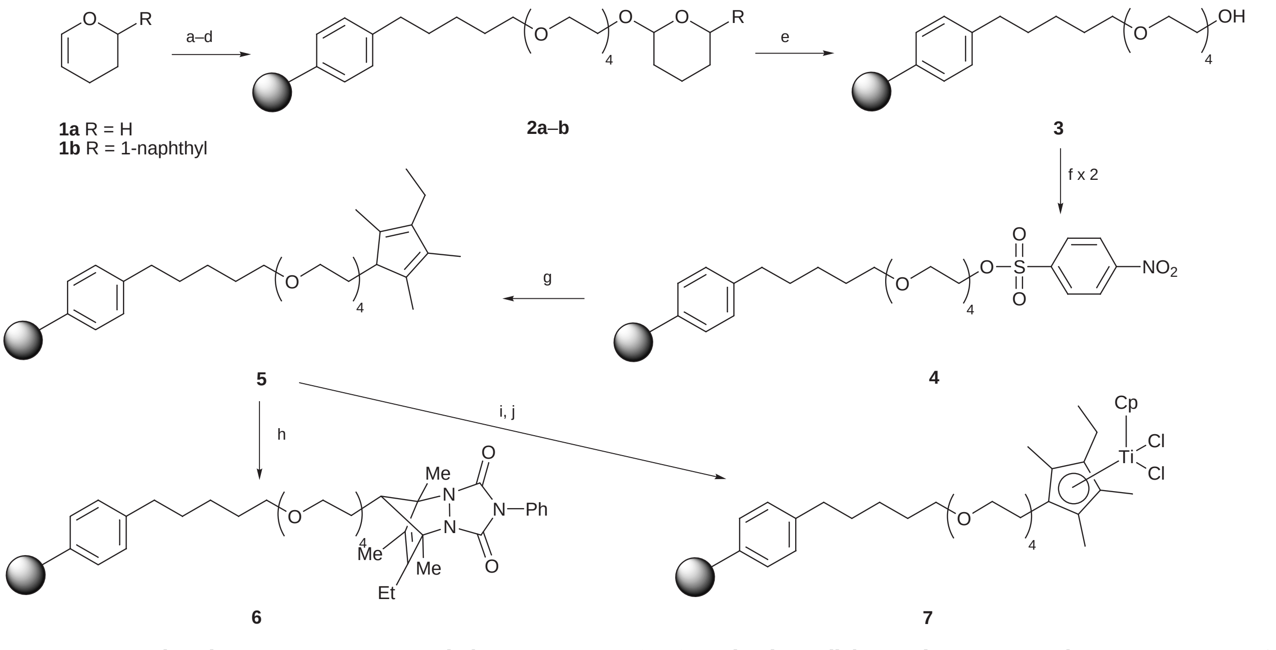
A spacer-modified polystyrene support with alcohol functionality was prepared using solid-phase organic reactions, and this resin was further derivatised to give a supported peralkylated titanocene which was active in ethylene polymerisation.

The rapid growth in combinatorial chemistry[1] has generated interest in the development of novel polymers, spacers and linkers for the adaptation of well-known solution methodologies to the solid phase. Transition metal catalysts anchored onto insoluble supports have also received much attention[2] as they are of great use in industrial scale processes, facilitating purification and catalyst recycling. So far, the use of supports for the latest generation of olefin polymerisation catalysts has mainly involved preadsorption of metallocenes on MAO-coated silica[3] or MCM-41.[4] The silica-based catalysts have been successfully used in large scale processes and the polymers obtained appear to be enlarged replicas of the original grains. However catalyst leaching can occur and neither are ideal supports for these unstable catalysts which are subject to facile deactivation. New ways to covalently attach metallocenes and to characterise the resulting complexes are needed, so that superior catalysts may be developed. The recent report by Frechet *et al.*[5] on the preparation of polyolefin spheres and related earlier studies prompts us to report our own work on supported metallocene catalysts.

The objectives of our investigations were to develop a new support **3** for solid-phase chemistry (Scheme 1) that would contain a spacer covalently attached to the resin *via* a stable C–C bond, with an alcohol end group, and to convert it into a well-defined supported titanocene **7**. Grubbs *et al.* have previously reported[6] polymer immobilised Ti-centred metallocene species, but have used these only as the basis of alkene hydrogenation catalysts.

The synthesis of the spacer unit was carried out in solution by sequential monoprotection of tetraethylene glycol (TEG) and monoalkylation with excess 1,5-dibromopentane (Scheme 1). The resulting bromide was attached onto the gel polystyrene support, by alkylation with polystyryllithium, prepared from *p*-bromopolystyrene (Fluka; 1.2–1.3 mmol g^{-1}, 100–400 mesh, 2% DVB) and *n*-butyllithium.[7] The loading level of the desired alcohol resin **3** was estimated during removal of the protecting group from **2b** using UV spectroscopy. FT-IR microspectroscopy, microanalysis and gel phase MAS NMR spectroscopy were used to fully characterise the alcohol resin product **3**.† The derivatisation of this alcohol support **3** was also studied and compared to that of some commercial supports. The nosylate derivative **4** was successfully prepared by treatment with excess 4-nitrobenzenesulfonyl chloride twice. Single bead FT-IR microspectroscopy and microanalysis (%N) were used to determine the extent of conversion. The reaction of the nosylate resin **4** with the tetraalkyl cyclopentadienyl anion was easily monitored by FT-IR and microanalysis (0%N), and gave the peralkylated cyclopentadienyl ligand **5**. The loading level of the cyclopentadienyl resin **5** was estimated by derivatisation with Cookson's reagent,[8] and %N analysis and FT-IR microspectroscopy of the resulting Diels–Alder adduct **6**.

The polymer-supported ligand **5** was converted into the titanocene complex **7** by deprotonation and reaction with cyclopentadienyltitanium trichloride. The titanium content of the beads was determined using inductively coupled plasma-atomic emission spectroscopy. The diffuse reflectance far-IR spectrum of the resin-bound catalyst **7** showed new sharp peaks in the region of 200–400 cm^{-1}, which are typical for Ti–Cl



Scheme 1 *Reagents and conditions*: a, TEG, CSA, CH$_2$Cl$_2$; b, NaH, THF; c, Br(CH$_2$)$_5$Br; d, polystyryllithium, toluene, 65 °C, 24 h; e, CSA, THF–H$_2$O, Δ; f, *p*-O$_2$NPhSO$_2$Cl, pyridine, DCM; g, NaCpMe$_3$Et, THF; h, Cookson's reagent, −78 °C, CH$_2$Cl$_2$; i, MeLi, THF; j, CpTiCl$_3$, toluene

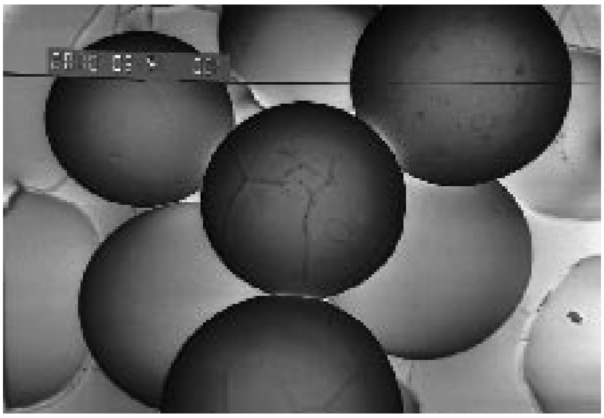


Fig. 1 SEM image of catalyst-containing beads **7**

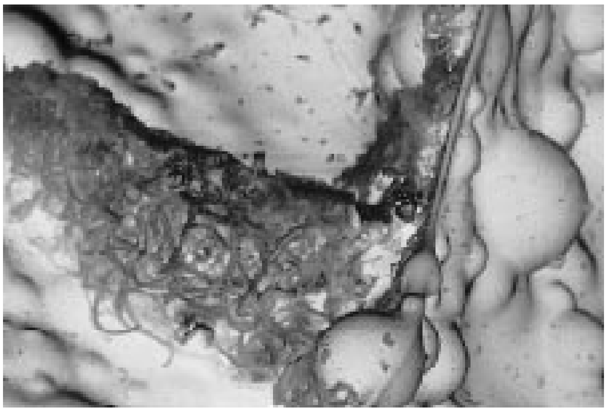


Fig. 2 SEM image of noodle-like polyethylene

stretches.[6] X-Ray photoelectron spectroscopy of a single bead gave a peak for the Ti 2p binding energy (at 457.5 eV) which is identical to that reported for other titanocene dichloride complexes.[9] This was good evidence that the structure of the species on the polymer was indeed analogous to that of the homogeneous catalyst. Scanning electron microscopy showed that the overall condition of the beads **7** (Fig. 1) was excellent. The chemical composition of the beads was also confirmed by X-EDS (X-ray energy dispersive spectroscopy) of clusters of beads. Analysis of the sample showed the presence of chlorine (Cl-Kα line = 2.6 keV) and titanium (Ti-Kα line = 4.5 keV) and the Cl : Ti ratio was roughly 2 : 1; in agreement with the catalyst structure.

This resin-bound complex **7** was tested for polymerisation activity by treatment with MAO (10^3 equiv.) and ethylene gas. The activity per bar per hour was estimated to be 41 g polyethylene per mmol catalyst, which was not as high as expected, probably due to diffusion problems into the active sites within the bead. The resulting noodle-like polyethylene chains emanating from the beads could be directly observed by scanning electron microscopy (SEM; see Fig. 2).‡ Kaminsky's work[10] on the coating of cellulose also described noodle-like morphology and it has been suggested that this only formed on very active catalytic centres. The high local activity of these centres on the polystyrene beads **7** could be due to site-isolation of the active species.

In conclusion, we have successfully prepared an active polymer-bound metallocene catalyst for olefin polymerisation. The full characterisation of this catalyst was made possible by the use of many new analytical techniques for on-the-bead characterisation as well as some novel monitoring methods for solid-phase reactions.§

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Note added at proof: Subsequent to the submission of this manuscript, Gibson and co-workers have reported the use of a polystyrene imidovanadium catalyst system for the polymerisation of ethylene: M. C. W. Chan, K. C. Chew, C. I. Dalby, V. C. Gibson, A. Kohlmann, I. R. Little and W. Reed, *Chem. Commun.*, 1998, 1673.

Notes and References

† Selected data for **3**: δ_C 71, υ_{max} 3300–3600 cm^{-1}, 0.5–0.8 mmol g^{-1}; for **4**: υ_{max} 1534, 1349 cm^{-1}, 0.21 mmol g^{-1}; for **5**: 0% N, 0.21 mmol g^{-1}; for **6**: υ_{max} 1718 cm^{-1}, 0.28 mmol g^{-1}; for **7**: see above, 0.07 mmol g^{-1}.

‡ GPC of the polymer was also performed (by extracting PE with trichlorobenzene at 160 °C) and showed a molecular weight peak at 734000 [M_n 358000, M_w 872000] and a polydispersity value (M_w/M_n) of 2.4. The M_n and polydispersity values were similar to those obtained from the soluble titanocene dichloride catalyst[10] [M_n 400000; M_w/M_n 2].

§ Taken from the PhD Thesis of Yolanda R. de Miguel, Imperial College, London 1997.

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