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Synthesis and characterization of a new polymer support for a metallocene catalyst

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Abstract—The synthesis of a novel polymer support and its use for the attachment of a metallocene catalyst is described in detail. The support was prepared by solid-phase synthesis from functionalized beads by the introduction of a spacer chain followed by the attachment of an alkylated cyclopentadienyl ligand. The characterization of the resulting resin-bound ligand and catalyst was achieved by using a wide range of analytical techniques for on-bead analysis. The supported titanocene complex exhibited moderate catalytic activity in the polymerization of ethylene. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

In recent years, there has been rapid growth in the development of novel polymer-supported compounds,[1] such as supported catalysts, reagents and scavengers. These insoluble species allow for rapid and simplified purification procedures and their use has become widespread in solution-phase organic synthesis and combinatorial chemistry.[2] Research in this field has also led to a greater demand for polymeric supports[3] that can withstand harsh reaction conditions. These can be prepared by co-polymerization of functionalized monomers or by post-polymerization modification of existing resins. One of the most active areas of research in the field of supported catalysis is the immobilization of catalysts for olefin polymerization.[4] The earliest supported metallocene catalysts developed for ethylene polymerization were based on silica particles, but this is not an ideal support for these catalysts due to the free hydroxyl groups on the surface which can lead to catalyst deactivation. The development of polystyrene-bound ethylene polymerization catalysts is currently an area of considerable interest, and many recent reports have concentrated on well-defined polystyrene-supported catalysts for olefin polymerization.[5] Herein we report our detailed studies on a novel synthetic route to prepare a polymeric support and demonstrate its use for the attachment of an ethylene polymerization catalyst.[6]

2. Results and discussion

The first objective of our investigation was to develop a new support **6** with alcohol functionality (Scheme 1) that would contain a flexible spacer chain. This chain would consist of methylene and ethylene glycol units, and would be covalently attached to the resin backbone via a stable C–C bond. The metallocene catalyst could be immobilized onto polystyrene in a number of ways,[4] however, we chose to use the covalent attachment of the metal catalyst via the η^5-cyclopentadienyl ligand. Therefore, our ultimate objective was to prepare a novel polymer-supported cyclopentadienyl ligand **9**, by derivatization of the alcohol resin **6**, which would be useful as a support for transition metal catalysts. This new ligand would be used to support the titanocene complex and lead to the generation of a new supported ethylene polymerization catalyst.

The preparation of the novel polymer support **6** required the synthesis of a suitably functionalized spacer chain **3a**. Its preparation was carried out in solution by monoprotection of tetraethylene glycol with dihydropyran **1a**, followed by deprotonation of the resulting alcohol **2a** and treatment with excess 1,5-dibromopentane (Scheme 1). The desired tetrahydropyranyl-protected bromide spacer **3a** could be easily prepared in large quantities and was obtained in good yield. Its attachment onto the polystyrene support was achieved by alkylation with polystyryllithium **4**, which was in turn prepared by a previously reported method[7] from polystyryl bromide by lithium–halogen exchange. The lithiation step could be monitored by bromine analysis of the beads **5a**. However, the need to determine the loading level of the final alcohol resin **6** (upon deprotection of **5a**) led to the development of a novel naphthyl-substituted tetrahydropyranyl

Keywords: polystyrene resin; polymer support; solid-phase organic synthesis; supported metallocene catalyst; ethylene polymerization.

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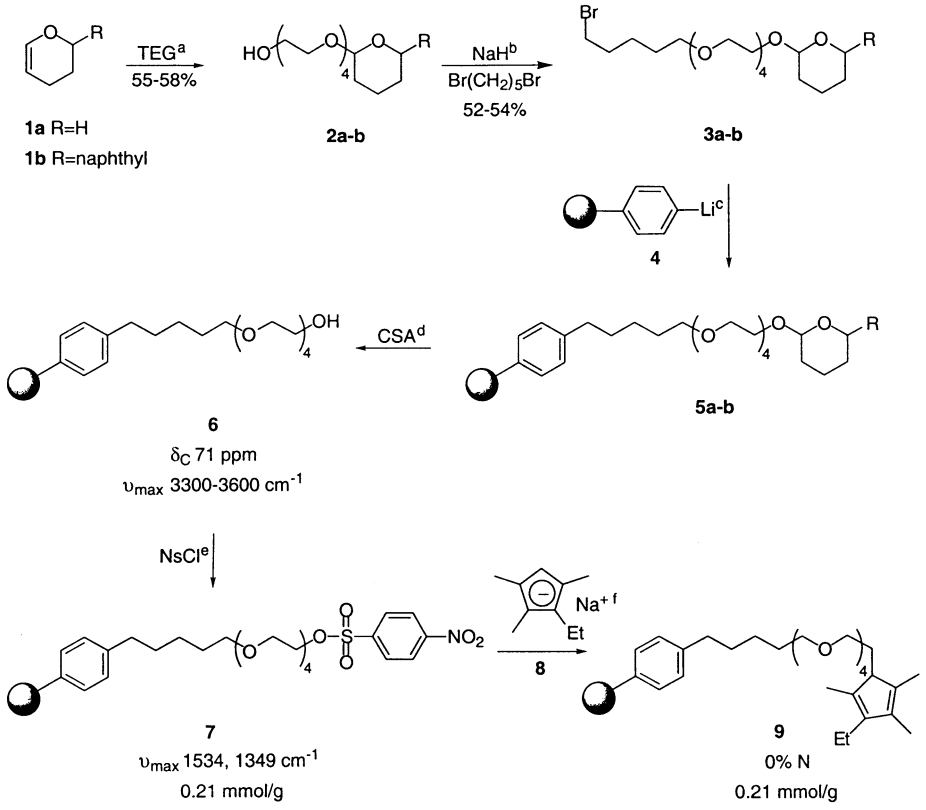
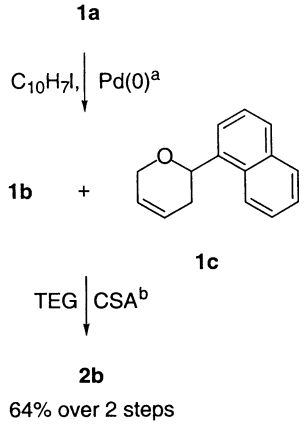


Scheme 1. *Reagents and conditions*: (a) $HOCH_2(CH_2OCH_2)_3CH_2OH$, CSA, CH_2Cl_2; (b) NaH, THF, $Br(CH_2)_5BR$; (c) **4**, PhMe, 65°C, 24 h; (d) CSA, THF, H_2O, Δ; (e) 4-$O_2NC_6H_4SO_2Cl$, pyridine, CH_2Cl_2; (f) **8**, THF. All reactions carried out at room temperature unless otherwise noted.

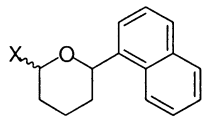
ether protecting group **1b** (Scheme 2) that would allow quantitative monitoring of the deprotection step by UV spectroscopy.

The palladium-catalyzed arylation[8] of dihydropyran **1a** to give the desired naphthyl derivative **1b** was investigated. This reaction gave a 1:1 mixture of regioisomers, **1b** and **1c**, which were separated by column chromatography. However, the optimized synthetic route involved treatment of the mixture (without the need for separation) with tetraethylene glycol to yield the intermediate **2b**, in high yield over the two synthetic steps. Deprotonation of the alcohol

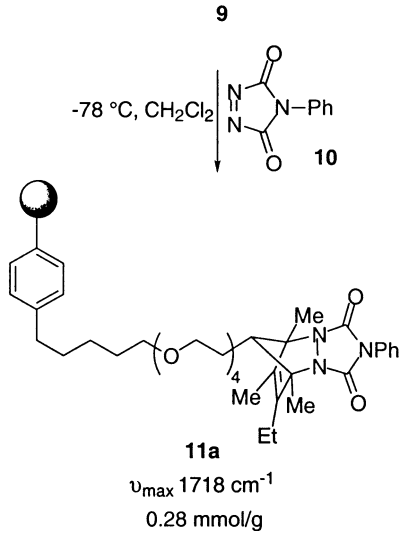


Scheme 2. *Reagents and conditions*: (a) 1-Iodonaphthalene, 2 mol% $(Ph_3P)_2Pd(OAC)_2$, Et_3N, 100°C, 48 h; (b) $HOCH_2(CH_2OCH_2)_3CH_2OH$ (TEG), CSA, CH_2Cl_2.

2b and selective monoalkylation of the 1,5-dibromopentane was achieved as before in moderate yield (54%) to give the desired naphthyl-containing bromide spacer **3b** (Scheme 1) which was treated with polystyryllithium **4** to give the protected intermediate **5b**. The cleavage of the protecting group initially resulted in the formation of a mixture of dihydropyran **1b** and hydroxy-tetrahydropyran **1d**, which was treated with ethanol in order to force the complete conversion of both species to adduct **1e**. This process was easily monitored by GC–MS, while UV spectroscopy of the final cleaved species **1e** was used to estimate the loading of the alcohol resin **6**. At this stage, FT-IR microspectroscopy was used to detect the presence of the alcohol group in the resin **6**. In addition, the ^{13}C and ^{1}H Gel Phase MAS NMR spectra of this resin contained the expected peaks at δ 71 and 3.8 ppm, respectively, for the ethylene glycol moiety.



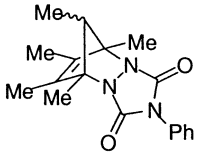
The nosylate derivative **7** was successfully prepared from the alcohol beads **6** (Scheme 1) by two sequential treatments with excess 4-nitrobenzenesulfonyl chloride. Examination of these beads by single bead FT-IR microspectroscopy showed the appearance of two new peaks, due to the nitro group, as well as disappearance of the hydroxyl peak. The reaction progress could therefore be monitored by removal



Scheme 3.

of sample beads from the reaction vessel, followed by washing with dichloromethane and drying prior to IR spectroscopic examination. Microanalysis (% nitrogen) was also used to determine the extent of conversion and the loading level (0.21 mmol g^{-1}). The reaction of the nosylate resin **7** with the ethyl(trimethyl)cyclopentadienyl anion **8**, freshly prepared by deprotonation of the alkylated cyclopentadiene[9] with sodium hydride, was easily monitored by FT-IR (disappearance of the nitro peaks) and microanalysis (0% nitrogen). The polymer-bound peralkylated cyclopentadienyl ligand **9** was thus obtained. It was initially assumed that all the nosylate had been displaced by the anion, so there would be an equivalent loading of this ligand (0.21 mmol g^{-1}), however a derivatization reaction was also studied in order to confirm this result.

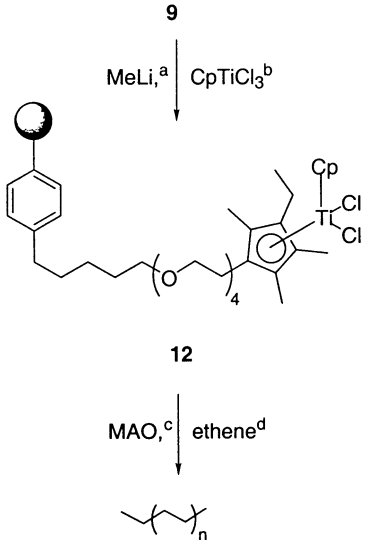
The loading level of the cyclopentadienyl resin **9** was indirectly estimated by derivatization with Cookson's reagent[10] **10** (Scheme 3) to give the Diels–Alder adduct **11a**. Addition of the highly reactive dienophile **10** (red color) at −78°C to the hindered resin-bound diene **9** resulted in decoloration of the reagent and formation of the supported adduct **11a**. This conversion could be followed by % nitrogen microanalysis and FT-IR microspectroscopy (appearance of a new carbonyl peak). A solution model experiment was carried out by treating pentamethylcyclopentadiene with Cookson's reagent **10** in the solution phase to yield the corresponding Diels–Alder adduct **11b**, which was fully characterized.



11 b

The loading level value for resin **9** obtained by derivatization with Cookson's reagent **10** was not identical, but was in the same range as the loading level which had been estimated from the nosylate displacement reaction (0.21 mmol g^{-1}). This disagreement was probably due to the indirect nature of both methods of quantitation, and the possibility of some side reactions in the derivatization of **9** with the Cookson's reagent **10**.

Finally, the polymer-anchored cyclopentadienyl ligand **9** was used to support a titanocene dichloride complex **12** (Scheme 4). Firstly, the resin-bound ligand **9** was deprotonated with methyllithium, followed by treatment of the anion with cyclopentadienyltitanium trichloride to give the desired product **12**. The titanium content of the beads was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and this allowed the estimation of the loading level of the catalyst (0.07 mmol g^{-1}). The diffuse reflectance far-IR spectrum of the resin-bound catalyst **12** (compared with that of the starting resin **9**) showed new sharp peaks in the region of 200–400 cm^{-1}, which are typical for Ti–Cl stretches. X-Ray photoelectron spectroscopy of a single bead showed a peak for the Ti 2p (at 457.5 eV) which is identical to that reported for other titanocene dichloride complexes.[11] This was good evidence that the structure of the species on the polymer was indeed analogous to the homogeneous catalyst. Scanning electron microscopy (SEM) showed that the overall condition of the beads **12** was excellent. The chemical composition of the beads was also confirmed by X-ray energy dispersive spectroscopy (X-EDS) of clusters of beads. Analysis of the sample showed the presence of chlorine (Cl K_α line= 2.6 keV) and titanium (Ti K_α line=4.5 keV) and the ratio of Cl/Ti was roughly 2:1; in agreement with the expected catalyst structure.



Scheme 4. *Reagents and conditions*: (a) MeLi, THF; (b) $CpTiCl_3$, PhMe; (c) MAO, PhMe, ethane; (d) HCl, MeOH.

Finally, this resin-bound complex **12** was tested for catalytic activity in the polymerization of ethene (Scheme 4). The polymer-supported titanocene dichloride **12** was first treated with a large excess of methylalumoxane co-catalyst (MAO) in toluene, to give the reactive catalytic species. Upon addition of ethylene gas, the formation of polyethylene was immediately observed. The activity per bar per hour was estimated to be 41 g PE/mmol catalyst, which was not as high as for previously reported catalysts. An interesting

observation was the presence of noodle-like polyethylene chains emanating from the beads that could be seen in the SEM image of the product. Kaminsky's work[12] on the coating of cellulose with polyethylene has also described this noodle-like morphology. GPC analysis of the polymer was also performed, by extracting the polyethylene with trichlorobenzene at 160°C, and showed a molecular weight peak at 734,000 (M_n 358,000, M_w 872,000) 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 (M_n 400,000; M_w/M_n 2).

3. Conclusions

This paper reports the synthesis of a spacer-modified polymer support with alcohol functionality **6** and its use in the preparation of a new polymer-bound peralkylated cyclopentadiene ligand **9**. This new support was also used to covalently attach a metallocene catalyst **12** that was successful in ethylene polymerization. Many new analytical techniques for on-bead characterization were used and some novel monitoring methods for solid-phase reactions, such as the UV-active tetrahydropyranyl ether protecting group, were also developed.

4. Experimental

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300, a JEOL GSX-270 or a Bruker AM-500 with NMR solvent as the internal standard. Gel phase ^{13}C NMR of solvent-swollen gels (in CD_2Cl_2) were recorded on a Bruker AM-500. ^{13}C and ^{1}H Gel Phase MAS NMR spectra were recorded on a Bruker MSL-300. IR spectra were recorded on a Mattson 5000 FT-IR spectrometer. Solid-state diffuse reflectance FT-IR spectra were recorded either neat or as KBr dispersions (using a KBr background). Single bead FT-IR spectra (transmittance) were recorded on the ATI Mattson (Infinity series 60MI) Quantum FT-IR microscope. GC–MS spectra were recorded on a Hewlett Packard 5890GC/5972MS spectrometer (helium; HP-5 capillary column: 25 m length). The GC method was: (T_o=50°C (2 min); T_f=250°C (5 min); rate=20°C min^{-1}). Bromine and chlorine microanalyses were carried out at UCL Analytical Services. ICP-AES analysis (%Ti) was carried out at the Geology Department at Imperial College on a Fisons ARL3580B, 1m vacuum spectrometer. X-Ray photoelectron spectroscopy was carried out at UCL. Electron microscopy studies were performed on a JEOL JSM-T200 scanning electron microscope (Materials Department, Imperial College). Secondary electron images (SEIs) were recorded at an accelerating voltage of 15 kV and backscattered electron imaging (BEI) at 15 or 25 kV. Qualitative analysis of the samples was achieved by X-ray dispersive spectrometry (X-EDS), recorded by analysis of four or five beads at 25 kV accelerating voltage using the Link 290 EDX microanalytical system. The polyethylene-containing sample was analyzed on a JEOL JSM-T220A. The sample was prepared by supporting on a cold mounting resin. The resin hardener and cold mounting powder were thoroughly mixed and the resulting solution was poured over the sample onto a 1″ mount and allowed to set at room temperature for 48 h. It was ground gently using 1200 SiC paper and polished with 3 μm×1 μm diamond polish, washed with methanol and dried.

Cyclopentadienyl titanium trichloride was obtained from Aldrich and used and stored in a glove box. Polystyryl bromide was obtained from Fluka (1.2–1.3 mmol g^{-1}, 7.8% Br, 100–400 mesh, 2% DVB). Cookson's Reagent **10** was purchased from Aldrich. Ethyltrimethylcyclopentadiene was prepared by the literature procedure.[9] All solvents and reagents were purified by standard procedures.

4.1.1. 3,6,9,12-Tetraoxa-12-(2-tetrahydropyranyl)dodecan-1-ol (2a). 3,4-Dihydropyran **1a** (6.28 g, 75 mmol) and tetraethylene glycol (65 mL, 376 mmol) in CH_2Cl_2 (200 mL) were cooled to 0°C and CSA (190 mg, 0.8 mmol) was added with stirring. The resulting mixture was left for 10 min at 0°C, allowed to warm to room temperature and monitored by GC–MS. A solution of brine (125 mL), saturated $NaHCO_3$ (125 mL) and H_2O (125 mL) were added to the mixture, and the product extracted with Et_2O (500 mL). The organic layer was separated and washed with brine (2×200 mL), dried over $MgSO_4$ and K_2CO_3 (1:1), filtered and evaporated in vacuo to give a clear oil (17.1 g). Chromatography (silica; hexanes/EtOAc/MeOH 60:35:5) gave **2a**[12] (12 g, 58%) as a clear oil: R_f 0.18 (hexanes/EtOAc/MeOH 60:35:5); IR (thin film) 3462 (br), 2939, 2870, 1455, 1350, 1125, 1076, 1035, 988, 872, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19–1.6 (m, 8H, CH_2), 2.91 (br, 1H, OH), 3.26–3.57 (m, 16H, CH_2O), 4.32 (t, J=3 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.7, 25.7, 30.8, 61.9, 62.4, 66.9, 70.6, 70.8, 70.87, 70.92, 72.9, 99.2; MS (CI) m/z 279 ([M+H]$^+$), 296 (100%, [M+NH$_4$]$^+$); GC–MS R_t 12.05 min. The material was used directly in the next step without further purification.

4.1.2. 2-(17-Bromo-3,6,9,12-tetraoxaheptadecan-1-lyoxy)-tetrahydropyran (3a). Alcohol **2a** (1.4 g, 4.7 mmol) in THF (10 mL) was added dropwise to a suspension of NaH (350 mg, 8.7 mmol) in THF (30 mL) cooled in an ice bath. The mixture was allowed to warm up to room temperature and stirred for 3 h. Stirring was stopped and the supernatant solution and THF washings (20 mL) were added slowly by cannula to 1,5-dibromopentane (24.9 g, 110 mmol) with stirring over 15 min. After the addition was complete, the mixture slowly turned milky white and was left at room temperature for 24 h. The mixture was diluted with CH_2Cl_2 (100 mL) and brine (100 mL) and the aqueous layer was extracted with CH_2Cl_2 (2×50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and evaporated in vacuo. Chromatography (silica; CH_2Cl_2/EtOAc/MeOH 90:9:1) gave **3a** (1.04 g, 52%) as a clear oil: R_f 0.23 (CH_2Cl_2/EtOAc/MeOH 90:9:1); IR (thin film) 2938, 2867, 1454, 1350, 1284, 1252, 1201, 1125, 1077, 1035, 988, 872, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43–2.3 (12H, m, CH_2–C), 3.32–3.82 (m, 22H, CH_2–O and CH_2–Br), 4.56 (t, J=3 Hz, 1H, O–CH–O); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 24.7, 25.3, 28.6, 30.4, 32.4, 33.5 (CH_2), 62.0, 66.5, 70.0, 70.3, 70.4 (coincident), 70.8, 76.5, 76.9, 77.4 (CH_2–O), 98.7 (O–CH–O); MS (CI) m/z 444, 446 ([M+NH$_4$]$^+$);

GC–MS R_t 18.49 min; HRMS (CI) calcd for $C_{18}H_{39}BrNO_6$: ($[M+NH_4]^+$), 444.1961; found: ($[M+NH_4]^+$), 444.2003. Anal. calcd for $C_{18}H_{35}BrO_6$: C, 50.59, H, 8.25. Found: C, 50.87; H, 8.21.

4.1.3. Polystyrene-supported THP ether (5a). *p*-Bromopolystyrene (0.97 g, 1.0 mmol) and *n*-BuLi (2.5 M in hexane; 3.3 mL, 8.2 mmol) in dry PhMe (20 mL) were heated at 65°C for 23 h. The solution was removed by cannula and fresh PhMe and *n*-BuLi were added as before. The mixture was further heated for 27 h. After removal of the supernatant solution by cannula, the dark brown polymer was washed thoroughly with PhMe and suspended in PhMe. Bromide **3a** (1.2 g, 2.8 mmol) in PhMe (5 mL) was added by cannula to the slurry of polystyryllithium **4** in PhMe, and a fast color change to orange was observed. The mixture was further stirred at 65°C for 24 h. The polymer was filtered, washed thoroughly with H_2O, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 100 mL) and dried in vacuo (50°C, 0.1 mm, 4 days) to give **5a** (0.76 g) as orange beads: IR (diffuse reflectance) 3060, 3029, 2923, 2888, 2849, 1945, 1873, 1803, 1746, 1601, 1491, 1450, 1366, 1325, 1248, 1183, 1123, 1073, 1029, 907, 839, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) δ 1.58, 1.99, 3.76 (CH_2O), 5.60 (br), 5.99, 6.15, 6.47, 6.64, 6.65, 6.68, 7.15; ^{13}C NMR (125 MHz, CD_2Cl_2, gel phase MAS) δ 14.2, 14.3, 20.0, 22.7, 25.9, 30.1, 31.1, 34.5, 40.9, 43–45, 67.2, 70.7 (strong, C–O), 99.5, 126.1, 128.2. Anal. found: C, 86.50; H, 7.88; N, 0.00; Br, 3.96.

4.1.4. Polystyrene-supported alcohol resin (6). A mixture of polymer **5a** (0.35 g, 0.35 mmol) and CSA (0.28 g, 1.2 mmol) in THF (10 mL) and H_2O (0.5 mL) was shaken at room temperature for 5 days, filtered and thoroughly washed with H_2O, aqueous MeOH, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 100 mL), and dried in vacuo to give **6** (0.31 g) as a pale yellow solid: IR (solid-state) 3473 (br), 3064, 3022, 2922, 2889, 2843, 1942, 1873, 1803, 1745, 1666, 1601, 1543, 1489, 1446, 1375, 1329, 1246, 1182, 1153, 1111, 1072, 1030, 964, 906, 841, 757, 700, 690, 547, 532 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) δ 0.13, 0.15, 1.59, 2.01, 3.59, 3.73, 3.79 (CH_2O), 6.65, 7.16; ^{13}C NMR ($CDCl_3$, 75 MHz, gel phase MAS) δ 0.8, 14.9, 23.2, 26.7, 30.3, 32.3, 34.4, 36.3, 41.2, 42.6, 44.6, 46.8, 62.4, 71.4 (strong, C–O), 72.3, 73.5, 80.9, 100.8, 104.0, 104.9, 118.1, 140.4, 146.1, 154.2, 156.4, 168.2, 173.8. Anal. found: C, 86.58; H, 7.93; N, 0.00.

4.1.5. Polystyrene-supported 4-nitrobenzenesulfonate resin (7). Pyridine (0.2 mL, 2.5 mmol) was added dropwise to a mixture of polymer **6** (0.22 g, 0.2 mmol) and 4-nitrobenzenesulfonyl chloride (187 mg, 0.84 mmol) in CH_2Cl_2 (10 mL). The mixture was shaken at room temperature for 3 days, filtered and the polymer washed thoroughly with H_2O, THF, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 50 mL), dried in vacuo to give **6/7** (200 mg) as pale yellow beads. The polymer was allowed to react again with 4-nitrobenzenesulfonyl chloride (200 mg, 0.9 mmol) and pyridine (0.2 mL, 2.5 mmol) in CH_2Cl_2 (20 mL) and further shaken for 5 days. The polymer **7** was purified as before to give pale brown beads (170 mg): IR (solid-state) 3071, 3037, 2875, 1946, 1874, 1803, 1747, 1669, 1600, 1526, 1491, 1445, 1350, 1204, 1120, 1029, 963, 909, 848 cm^{-1}. Anal. found: C, 86.03; H, 7.87; N, 0.30 (0.21 mmol g^{-1}).

4.1.6. Sodium ethyltrimethylcyclopentadienide (8). A solution of the tetraalkyl cyclopentadiene[9] (0.4 g, 3 mmol) in THF (10 mL) was added slowly, by cannula, to an ice-cooled suspension of NaH (0.19 g, 4.7 mmol) in THF (10 mL). The mixture was stirred at room temperature for 4 h and filtered by cannula for immediate use.

4.1.7. Polystyrene-supported peralkylated cyclopentadiene (9). A solution of sodium ethyltrimethylcyclopentadienide **8** (0.06 M in THF, 15 mL, 0.9 mmol) was added slowly, by cannula, to a suspension of polymer **7** (0.21 mmol g, 0.14 g, 0.03 mmol) in THF (1 mL). The resulting mixture was shaken at room temperature for 7 days, filtered and the polymer washed thoroughly with H_2O, THF, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 50 mL) and dried in vacuo to give **9** (91 mg) as brown beads: IR (solid-state, diffuse reflectance, neat) 3059, 3028, 2923, 2852, 1944, 1872, 1803, 1745, 1667, 1601, 1492, 1449, 1371, 1328, 1184, 1115, 1070, 1028, 907, 841 cm^{-1}; IR (solid-state, transmittance, polystyrene background) 1600, 1492, 1453, 1367, 1244, 1185, 1122, 1028, 842, 772 cm^{-1}; IR and FAR-IR (diffuse reflectance, CsI dispersion) 1598, 1494, 1457, 1382, 1315, 1182, 1072, 1027, 966, 906, 840, 771, 707, 620 and 541 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) −0.33, 0.03, 0.24, 1.58, 3.41 and 6.72; ^{13}C NMR ($CDCl_3$, 75 MHz, gel phase MAS) 0.9, 14.7, 23.1, 26.4, 30.2, 41.1, 42.4, 44.3, 102.7, 120.0, 126.3, 128.4, 146.0, 151.8, 153.9, 171.6, 179.6. Anal. found: C, 87.06; H, 7.12; N, 0.0 (0.21 mmol g^{-1}).

4.1.8. 2-(1-Naphthyl)-3,4-dihydro-2*H*-pyran (1b). 1-Iodonaphthalene (2.5 mL, 11.5 mmol), dihydropyran **1a** (17 mL, 186 mmol), Et_3N (3.4 mL, 25.4 mmol) and $(Ph_3P)_2PdCl_2$ (208 mg, 0.28 mmol, 2 mol%) were degassed (freeze-pump-thaw twice) and heated in a sealed tube at 100°C for 48 h. GC–MS analysis showed no starting material and a mixture of isomeric products. The cooled reaction mixture was extracted with CH_2Cl_2 (50 mL), washed with H_2O (2×50 mL) and the organic extracts were evaporated in vacuo to give an orange oil. The crude product was redissolved in pentane, filtered, evaporated in vacuo and chromatographed (silica, pentane) to give **1b/1c** (2.43 g, 100%). Chromatography (silica, pentane) gave isomer **1b** (1.4 g, 58%) as a clear oil: R_f 0.18 (pentane); IR (thin film) 3057, 2922, 1647, 1240, 1058, 797, 779, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.0–2.4 (m, 4H), 4.86 (m, 1H), 5.55 (d, J=9 Hz, 1H), 6.64 (d, J=6 Hz, 1H), 7.2–8.0 (7H, m, 7H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 30.1, 74.8, 101.3, 123.4, 123.7, 125.9, 126.5, 128.6, 129.4 (7 Ar CH), 130.8, 134.2, 137.8 (3 Ar C), 145.0; MS (CI) *m/z* 211 (86%, $[M+H]^+$), 228 (100%, $[M+NH_4]^+$); GC–MS R_t 11.74 min; HRMS (CI) calcd for $C_{15}H_{14}O$+H: ($[M+H]^+$), 211.1123; found: ($[M+H]^+$), 211.1114. Anal. calcd for $C_{15}H_{14}O$: C, 85.68, H, 6.71. Found: C, 85.84; H, 6.91.

4.1.9. 2-(1-Naphthyl)-3,6-dihydro-2*H*-pyran (1c). 1-Iodonaphthalene (0.6 mL, 4.1 mmol), 3,4-dihydropyran **1a** (4 mL, 44 mmol), Et_3N (0.8 mL, 5.7 mmol) and bis(triphenylphosphine)palladium diacetate (44 mg, 0.06 mmol, 1 mol%)

were degassed (freeze-pump-thaw twice) and heated in a sealed tube at 100°C for 24 h. The cooled reaction mixture was extracted with CH_2Cl_2 (30 mL), washed with H_2O (2×50 mL), and the organic extracts were evaporated in vacuo to give an orange oil. Chromatography (silica, pentane) gave isomer **1c** (0.37 g, 42%) as a clear oil: R_f 0.09 (pentane); IR (thin film) 3038, 2926, 2824, 1655, 1597, 1511, 1388, 1338, 1235, 1179, 1091, 1023, 919, 799, 777, 659 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32–2.55 (m, 2H), 4.32–4.48 (m, 2H), 5.20 (dd, J=3.7, 9.4 Hz, 1H), 5.79–5.96 (m, 2H), 7.34–8.05 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.7, 65.3, 71.7, 121.8, 122.0, 123.3, 124.0, 124.1, 124.5, 125.0, 126.6, 127.4 (7 Ar+2 alkene CH), 129.1, 132.3, 136.6 (3 Ar C); MS (CI) m/z 211 (57%, $[M+H]^+$), 228 (100%, $[M+NH_4]^+$); GC–MS R_t 11.88 min; HRMS (CI) calcd for $C_{15}H_{14}O+H$: ($[M+H]^+$), 211.1123; found: ($[M+H]^+$), 211.1125. Anal. calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.49; H, 6.91.

4.1.10. 3,6,9,12-Tetraoxa-12-(2-(6-(1-naphthyl))-2-tetrahydropyran-1-yl)-dodecan-1-ol (2b). Dry CSA (200 mg, 0.8 mmol) was added to crude 2-naphthyl-dihydropyran **1b** and **1c** (2.5 g, 11.5 mmol) and tetraethylene glycol (5.5 mL, 32 mmol) in CH_2Cl_2 (40 mL), The resulting mixture was left at room temperature overnight. The mixture was washed with brine, saturated aqueous $NaHCO_3$ and H_2O (20 mL each) and extracted with CH_2Cl_2 (2×20 mL). The organic layer was separated, washed with brine (30 mL), dried over $MgSO_4$, filtered and evaporated in vacuo gave **2b** as a mixture of diastereoisomers. Chromatography (silica, hexanes/EtOAc/MeOH 65:30:5) to give **2b** (2.93 g, 64% from **1a**) as a clear oil: R_f 0.14 (hexanes/EtOAc/MeOH 65:30:5); IR (thin film) 3465 (br), 3050, 2937, 2872, 1597, 1511, 1455, 1350, 1122, 1072, 1037, 982, 801, 780 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71–2.01 (m, 6H), 2.73 (br, 1H, OH), 3.56–3.9 (m, 16H, 8×CH_2O), 5.12 (s, 1H), 5.60 (dd, J=2, 11 Hz, 1H), 7.26–8.14 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 29.8, 33.2, 61.8, 66.7, 68.1, 70.4, 70.7 (coincident CH_2O), 72.5, 98.4, 123.3, 123.4, 125.3, 125.6, 125.7, 127.6, 128.9, 130.5, 133.8, 139.0; MS (CI) m/z 422 (100%, $[M+NH_4]^+$); HRMS calcd for $[C_{23}H_{32}O_6+NH_4^+]$: ($[M+NH_4]^+$), 422.25426; found: ($[M+NH_4]^+$), 422.2538. Anal. calcd for $C_{23}H_{32}O_6$: C, 68.28, H, 7.98. Found: C, 68.11; H, 7.85.

4.1.11. 2-(17-Bromo-3,6,9,12-tetraoxaheptadecan-1-yl-oxy)-6-(1-naphthyl)-tetrahydropyran (3b). Alcohol **2b** (2.37 g, 5.8 mmol) in THF (50 mL) was added dropwise to an ice-cooled suspension of NaH (0.65 g, 16 mmol) in THF (50 mL). The resulting mixture was allowed to warm to room temperature and stirred for 20 h. The supernatant solution was decanted by cannula and added dropwise to 1,5-dibromopentane (25 mL, 183 mmol). The solution went cloudy and NaBr precipitated overnight. The mixture was diluted with CH_2Cl_2 and H_2O, and the aqueous layer was extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were washed with brine (2×25 mL), dried over Na_2SO_4, filtered and evaporated in vacuo. The crude oil was filtered through a large plug of silica with CH_2Cl_2 to remove excess 1,5-dibromopentane and with EtOAc to yield **3b** as a clear oil. Chromatography (silica; hexanes/EtOAc/MeOH 60:35:5) gave **3b** (1.74 g, 54%) as a mixture of diastereoisomers. The partial separation of the diastereoisomers (R_f 0.61, 0.69 (hexanes/EtOAc/MeOH 60:35:5)) was achieved giving samples of each both as clear oils. The less polar isomer of **3b** (R_f 0.61) showed: IR (thin film) 3050, 2938, 2863, 1597, 1455, 1350, 1296, 1241, 1202, 1118, 1073, 1029, 983, 859, 800, 779, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18–1.96 (m, 12H), 3.30–3.95 (m, 20H), 4.72 (dd, J=2.0, 9.5 Hz, 1H), 5.08 (dd, J=9.7 Hz, 1H), 7.19–7.96 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.8, 25.8, 29.7, 32.1, 32.9, 33.5, 34.6, 68.8, 71.1, 71.5 (coincident), 72.0, 75.8, 104.2, 124.1, 126.2, 126.5, 126.7, 128.8, 129.8; MS (CI) m/z 210 (100%, M−343), 572 (71%, $[M+NH_4]^+$); HRMS (CI) calcd for $C_{28}H_{45}NO_6Br$: ($[M+NH_4]^+$), 572.2439, 570.2450; found: ($[M+NH_4]^+$), 572.2410, 570.2430. Anal. calcd for $C_{28}H_{41}BrO_6$: C, 60.76, H, 7.47. Found: C, 60.47; H, 7.20.

4.1.12. Polystyrene-supported ether (5b). *p*-Bromopolystyrene (2.11 g, 2.1 mmol) and *n*-BuLi (2.5 M in hexane, 8.0 mL, 17.6 mmol) in PhMe (30 mL) were heated at 65°C for 28 h. The solution was removed by cannula and fresh PhMe and *n*-BuLi were added as before. The mixture was heated for 26 h, washed, re-treated with fresh reagents and the resulting dark polymer suspension was heated for a further 24 h. After removal of the supernatant solution by cannula, the dark brown-red lithiated polymer was washed thoroughly with dry PhMe (2×10 mL) and suspended in PhMe. A solution of the bromide **3b** (1.0 g, 1.81 mmol) in PhMe (5 mL) was added by cannula to the slurry of polystyryllithium **4** in PhMe, and a gradual color change to orange was observed. The mixture was heated at 65°C for 42 h and was left at room temperature for 24 h. The polymer was filtered, washed thoroughly with H_2O, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 100 mL) and dried in vacuo (50°C, 0.1 mm, 24 h) to give **5b** (1.85 g) as orange beads: IR (diffuse reflectance) 3078, 3062, 3024, 2939, 2908, 2848, 1944, 1873, 1803, 1745, 1666, 1601, 1495, 1452, 1373, 1329, 1246, 1180, 1155, 1115, 1072, 1028, 964, 943, 906, 839, 621, 542 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) δ 0.11, 0.13, 1.58, 1.98, 3.73 (CH_2O), 6.64, 7.15; ^{13}C Gel NMR (125 MHz, CD_2Cl_2) δ 0.8, 15.0, 23.2, 30.4, 41.2, 44.6, 46.7, 71.4 (strong, C–O), 73.3, 81.3, 99.1, 101.4, 104.1, 126.4, 128.5, 128.7, 146.02, 156.0, 173.4. Anal. found: C, 86.78; H, 7.67; Br, 4.13.

4.1.13. Procedure for UV monitoring of the deprotection of resin 5b: estimated loading level of alcohol resin 6. The protected polymer **5b** (1.21 g, 1.2 mmol) and CSA (0.89 g, 3.8 mmol) in THF (10 mL) and EtOH (7 mL) were shaken at room temperature for 24 h. The polymer was filtered off and thoroughly washed with THF (10 mL). Saturated aqueous $NaHCO_3$ solution was added dropwise to the filtrate until fizzing stopped and Et_2O (30 mL) was added. The aqueous layer was further extracted with Et_2O (2×30 mL) and the combined organic layers were dried over Na_2SO_4, filtered and evaporated in vacuo to give a solid residue (25 mg); UV λ_{max} (MeCN) 222 nm (absorbance corresponding to 0.1 mmol). Loading level ca. 0.1 mmol g^{-1}. The polymer was washed thoroughly with H_2O, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 100 mL) and dried in vacuo (50°C, 0.1 mm, 24 h) to give polymer **6** (1.12 g): IR (solid-state) 3400 (br), 3072, 3047, 3002, 2957, 2922, 2843, 1945, 1874, 1804, 1744, 1673,

1599, 1542, 1464, 1375, 1312, 1183, 1154, 1070, 964, 943, 908, 844, 777 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) δ −0.37, 0.16, 1.04, 1.60, 2.01, 3.78 (CH_2O), 6.65, 7.18; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.8, 14.9, 23.1, 29.6, 36.3, 41.1, 42.4, 44.4, 62.4, 69.3, 71.3 (C–O), 99.6, 107.2, 112.9, 117.1, 120.5, 126.4, 128.4, 146.0, 157.3, 174.9, 179.4. Anal. found: C, 87.96; H, 7.48; N, 0.00.

4.1.14. Characterization of cleavage product from polymer 5b: 2-ethoxy-6-(1-naphthyl)-tetrahydropyran (1e). Polymer **5b** (1.02 g, 2.5 mmol) and CSA (1.6 g, 7 mmol) in THF (60 mL) and H_2O (2 mL) were stirred at room temperature for 24 h. GC–MS analysis showed two products: dihydropyran **1b** (38%, $M^{+\cdot}$ 210) and tetrahydropyran **1d** (57%, $M^{+\cdot}$ 228). EtOH (10 mL) was added to the reaction mixture and the solution was left standing for 2 h. At this stage the only product detected by GC–MS was ether **1e** (100%, $M^{+\cdot}$ 256). Saturated aqueous $NaHCO_3$ solution was added until the effervescence stopped, and Et_2O (30 mL) was added. The aqueous layer was further extracted with Et_2O (30 mL) and the combined organic layers were dried over Na_2SO_4, filtered and evaporated in vacuo to give **1e** (0.63 g, 98%) as an oil. Chromatography (silica, hexanes; Et_2O/hexanes 5:95) gave samples of the two isomers as white solids R_f 0.26, 0.30 (pentane). The more polar isomer showed: mp 64–65°C; IR (CH_2Cl_2 film) 3052, 2977, 2947, 1372, 1266, 1125, 1064, 1029, 981, 801, 780, 739, 705 cm^{-1}; UV λ_{max} (MeCN) 224 nm (ε 76,000); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J=7 Hz, 1H, Me), 1.72–2.25 (m, 6H), 3.54 (m, 1H, methylene), 3.82 (m, 1H, methylene), 5.12 (br s, 1H), 5.61 (dd, J=2, 11 Hz, 1H), 7.46–8.15 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.3, 18.9, 30.0, 33.2, 62.7, 67.9, 97.8, 123.2, 123.4, 125.3, 125.7, 125.8, 127.7, 129.0, 130.4, 133.8, 139.0; MS (CI) m/z 274 (9%, $[M+NH_4]^+$), 256 (32%, M^+), 228 (100%, $[M+H-Et]^+$); GC–MS R_t 11.98 min; HRMS (CI) calcd for $C_{17}H_{24}NO_2$: ($[M+NH_4]^+$), 274.1807; found: ($[M+NH_4]^+$), 274.1805. Anal. calcd for $C_{17}H_{20}O_2$: C, 79.65, H, 7.86. Found: C, 79.59; H, 7.86.

4.1.15. Polystyrene-supported Diels–Alder adduct (11a). Cookson's reagent **10** (5 mg, 29 μmol) in CH_2Cl_2 (0.25 mL) was added dropwise to a cooled suspension of cyclopentadiene polymer **9** (10 mg, 2 μmol) in CH_2Cl_2 (0.25 mL). The resulting mixture was left at room temperature overnight, saturated aqueous $NaHCO_3$ solution was added and the polymer was collected by filtration, washed thoroughly with H_2O, THF, MeOH, Me_2CO, EtOAc, CH_2Cl_2 and pentane (all 50 mL) and dried in vacuo to give **11a** (8 mg) as brown beads: IR (solid-state, transmittance, neat) 3060, 3029, 2932, 2853, 1944, 1872, 1722, 1602, 1494, 1449, 1371, 1239, 1116, 1071, 1028, 907, 840 cm^{-1}; IR (solid-state, transmittance, polystyrene background) 1711, 1645, 1558, 1407, 1236, 1128 cm^{-1}. Anal. found: C, 82.45; H, 7.13; N, 1.17 (0.28 mmol g^{-1}).

4.1.16. Diels–Alder reaction of *N*-phenyl-1,3,4-triazoline-2,5-dione 10 with pentamethylcyclopentadiene. Cookson's reagent **10** (27 mg, 154 μmol) in CH_2Cl_2 (0.75 mL) was added dropwise to a solution of pentamethylcyclopentadiene (21.8 mg, 160 μmol) in CH_2Cl_2 (0.25 mL) at −78°C. The dark red color disappeared almost immediately and the resulting yellow solution was left at room temperature overnight. Filtration through a short pad of silica (CH_2Cl_2) and evaporation in vacuo gave **11b** (42 mg, 87%), a mixture of isomers (3:1), as a white solid: mp 105–109°C; R_f 0.76 (1:1 Et_2O/pentane); IR (CH_2Cl_2 film) 3056, 2977, 2937, 1768, 1712, 1599, 1501, 1442, 1401, 1266, 1141, 793, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, J=6.5 Hz, 3H, bridgehead Me, 72%), 0.98 (d, J=6.7 Hz, 3H, bridgehead Me, 28%),1.57 (q, J=6.5 Hz, 1H, bridgehead H, 28%), 1.73–1.78 (m, 12H, 4 Me), 2.13 (1H, q, J=6.5 Hz, bridgehead H, 72%), 7.30–7.43 (5H, m, ArH); ^{13}C NMR (CDCl3, 125 MHz) δ 7.9, 9.2, 10.9, 11.1, 12.9, 13.2, 29.7, 30.4, 60.4, 61.0, 78.7, 79.9, 125.4, 128.0, 128.1, 129.0, 131.6, 131.8, 135.5, 159.2, 159.6; MS (CI) m/z 312 (66%, $[M+H]^+$), 136 (100%, Cp); HRMS (CI) calcd for $C_{18}H_{21}N_3O_2$: ($[M+H]^+$), 312.1712; found: ($[M+H]^+$), 312.1700. Anal. calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49. Found: C, 69.34; H, 7.01; N, 13.79.

4.1.17. Polystyrene-supported titanocene dichloride complex (12). Polymer **9** (0.11 mmol g^{-1}, 1.08 g, 0.12 mmol) was suspended in THF (10 mL) and MeLi (1.5 M in Et_2O, 0.6 mL, 0.9 mmol) was added dropwise. The resulting mixture was shaken at room temperature for 3 days when the supernatant solution was removed by cannula. The beads were thoroughly washed with THF (10 mL) and PhMe (2×10 mL). Cyclopentadienyltitanium trichloride (54 mg, 0.25 mmol) in PhMe (10 mL) was added by cannula to the beads in PhMe (10 mL) and the suspension was shaken at room temperature for 6 days. The solution was completely removed as before and the resin was thoroughly washed with THF (2×40 mL) and PhMe (2×40 mL) and dried in vacuo overnight to give **12** (0.88 g) as orange-brown beads: TGA: residue 8.18%; IR and FAR-IR (diffuse reflectance, CsI dispersion) 1598, 1494, 1454, 1297, 1201, 1155, 1112, 1066, 1025, 977, 944, 906, 738, 700, 534, 464, 325, 264, 233, 208 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, gel phase MAS) δ 0.12, 0.14, 0.32, 1.56, 1.98, 2.45, 6.62, 7.15; ^{13}C Gel NMR (125 MHz, CD_2Cl_2) δ 0.8, 12.8, 14.9, 22.3, 41.1, 44.5, 69.2 (C–O), 99.8, 100.9, 118.3, 126.4, 128.5, 146.0, 156.2, 173.7. Anal. found: C, 85.66; H, 7.53; X (Br, Cl), 5.90; N, 0.00; Ti, 0.33 (0.07 mmol g^{-1} Ti).

4.2. Catalytic activity of polymer-supported titanocene dichloride (12) in the polymerization of ethene: preparation of polyethylene (PE)

Excess MAO (1.72 M in PhMe, 10 mL, 17 mmol) was added to a suspension of catalyst beads **12** (0.25 g, 17.5 μmol) in PhMe (50 mL) and the mixture was stirred for 30 min. Ethylene gas was added to the evacuated mixture at 20°C. The polymerization reaction was stopped after 1 h, as no more polymer appeared to be formed. The MAO was destroyed with a 10% HCl in MeOH, and the polymer was filtered and washed thoroughly with Me_2CO. After drying in vacuo at 50°C overnight, the product polyethylene–polystyrene (0.97 g) was obtained as a brown solid. This represents a mass of polyethylene of 0.72 g which corresponded to a catalytic activity of 41 g $mmol^{-1}$ bar^{-1} h^{-1}. DSC: T_1 142.25°C, T_2 169.48°C, T_3 450.34°C; GPC (7 mg in 25 mL trichlorobenzene, 160°C): M_n 358,000, M_w 872,000, M_w/M_n 2.4; peak 734,000.

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