Polystyrene supports for vanadium ethylene polymerisation catalysts

Michael C. W. Chan,[a] Kong Chin Chew,[a] Christopher I. Dalby,[a] Vernon C. Gibson,*[a]† A. Kohlmann,[a] Ian R. Little[b] and Warren Reed[b]

[a] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*
[b] *BP Chemicals, Sunbury Research Centre, Chertsey Road, Sunbury on Thames, Middlesex, UK TW16 7LN*

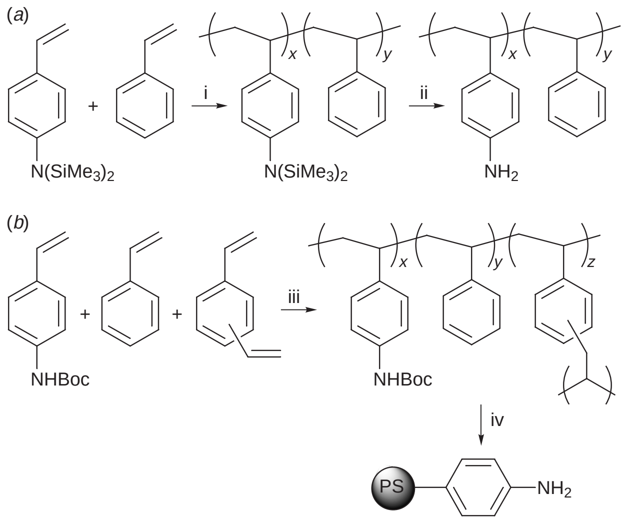
Amino-functionalised polystyrene resins have been synthesised and used as well-defined supports for imidovanadium ethylene polymerisation catalysts; a dramatic enhancement in the lifetime and productivity of the supported catalysts compared to their unsupported (homogeneous) analogues is found.

During the past decade there has been tremendous industrial and academic interest in the development of new generation, highly tunable catalysts for α-olefin polymerisation.[1] Advances in catalyst design, especially the development of well-defined 'single-site' systems,[2] and the technologically significant discovery of high performance cocatalysts such as methylaluminoxane (MAO),[3] have played a key role in driving this interest. A third and equally important component of industrially relevant catalyst systems, especially for those that operate in the gas phase, is the solid support to which the procatalyst and cocatalyst are often attached and through which the resultant polymer morphology may be controlled. A significant proportion of the world's supply of polyolefins is manufactured using catalysts supported on inorganic materials such as $MgCl_2$ (especially Ziegler-type catalysts)[4] or silica (especially chromium catalysts).[5] Silica especially is highly reactive due to the presence of surface hydroxy groups, even after prolonged calcination, and therefore is not particularly well-suited as a support for the latest generation well-defined catalyst systems which may undergo drastic chemical modification upon attachment to the SiO_2 surface. By contrast, inert organic supports can be synthesised with precision and control[6] and are readily functionalised in such a way as to allow a specific well-defined covalent linkage to be formed between the procatalyst, and possibly also the cocatalyst, and the support. Moreover, through free-radical suspension polymerisation methods, spherical polymer beads can be obtained of controlled size and porosity.[7] Carefully tailored organic supports thus offer a potentially significant development in the heterogenisation of well-defined homogeneous olefin polymerisation catalysts. Polystyrene resins impregnated with catalysts have been the focus of recent attention in industrial research laboratories[8] and covalently attached metallocenes have previously been investigated as hydrogenation catalysts.[9]

We describe herein the dramatic influence of an appropriately functionalised polystyrene on the kinetic profile of a model vanadium system. In previous work we have shown that complexes of the type $CpV(NR)Cl_2$ are active procatalysts for ethylene polymerisation.[10] However, it was found that they deactivate within minutes due to a reductive bimolecular decomposition process.[11] Recognising that isolating the active sites within an inert matrix should increase the longevity of this catalyst system, we targeted an appropriately functionalised polystyrene resin that would allow the organometallic procatalyst to be supported without loss of its integrity. In previous work, we have established that *tert*-butylimido ligands can be readily exchanged for arylimido groups upon treatment with an appropriate aniline.[11,12] This methodology offered an opportunity to (covalently) attach imidovanadium procatalysts to an inert organic support.

The amino-functionalised resins shown in Scheme 1 were targeted. The first samples were prepared *via* the living anionic polymerisation method reported by Nakahama and co-workers[13] [Scheme 1(*a*)] which involves silyl protection of the amino functionality followed by copolymerisation with styrene using sodium naphthalenide as an initiator. The resultant linear copolymers‡ were characterised by ^1H NMR spectroscopy and by GPC. The proportion of amino styrene in the polymer was determined by integration of the trimethylsilyl resonance (δ 0.05) *versus* the polystyryl backbone hydrogens. For this study we did not seek to obtain information concerning the uniformity of blockiness of the distribution of the aminostyryl units. After deprotection with HCl, the amino-functionalised polystyrene was treated with a toluene solution of $CpV(NBu^t)Cl_2$ for several days at 80 °C during which time the polymer took on the dark red coloration of the half-sandwich imido complex (Scheme 2). This supported procatalyst was then tested for ethylene polymerisation in a 1 l reactor; the results are collected in Table 1.

For comparison purposes, entry 1 shows the result of a polymerisation experiment using unsupported $CpV(NBu^t)Cl_2$ which, in combination with diethylaluminium chloride (DEAC) cocatalyst, is short-lived (<10 min) and affords a catalyst productivity of 6.8 g $mmol^{-1}$ h^{-1}. By contrast, treatment of the polystyrene-supported procatalyst with DEAC at 50 °C in the presence of ethylene (10 atm) affords a catalyst productivity of 77.2 g $mmol^{-1}$ h^{-1}. Significantly, however, a steady rate of ethylene uptake ensues over the 60 min duration of the run and the polymer was obtained as a flocculent product rather than the stringy material obtained from homogeneous polymerisations.[10] The polyethylene product is unimodal, of relatively

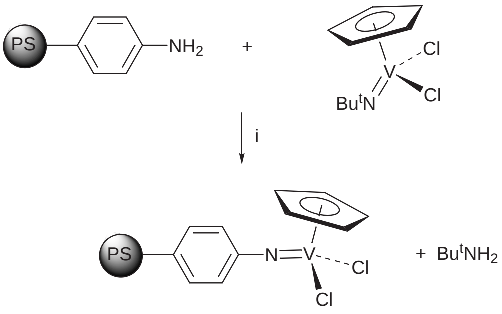


Scheme 1 *Reagents and conditions*: i, ii, ref. 13; iii, styrene, divinylbenzene, Boc-protected vinylaniline dissolved in chlorobenzene. The initiator AIBN (2 mol%) and monomer solution added to water (100 cm^3) containing calcium orthophosphate, calcium sulfate and poly(vinylpyrrolidone) as droplet stabilisers, stirring speed 200 rpm, 15 h; iv, HCl (aq) (12.6 M), THF, ultrasonic bath, 1 h

Table 1 Results of ethylene polymerisation

Run	Procatalyst[a]	Aminostyrene (mol%)	Activator (equiv.)	Ethylene pressure/atm	T/°C	t/min	Yield/g	Productivity§/ g mmol^{-1} h^{-1}
1	CpV(NBu^t)Cl$_2$ (unsupported)	—	DEAC (40)	10	50	60	1.00	6.8
2	PS–N=VCpCl$_2$	6.3	DEAC (34)	10	50	60	10.8	77.2
3	PS–N=VCpCl$_2$	6.3	DEAC (34)	10	75	60	1.9	13.7
4	PS–N=VCpCl$_2$	6.3	MAO (1000)	10	50	60	11.4	81.4
5	PS′–N=VCpCl$_2$	4.5	DEAC (20)	1	25	60	2.1	10.7

[a] PS = linear styrene–*p*-aminostyrene copolymer: PS′ = polystyrene–*p*-aminostyrene beads.



Scheme 2 *Reagents and conditions*: i, toluene, 80 °C, 9 d

high molecular weight (M_w 1.9 × 10^6, M_n 3.9 × 10^5) with little branching (< 1 per 5000 carbons) and with a molecular weight distribution (M_w/M_n) of 4.9. Raising the reactor temperature to 75 °C (entry 3) led to a reduction in productivity indicating that catalyst deactivation starts to become significant at elevated temperature. The use of a large excess of methylaluminoxane (MAO), in place of DEAC cocatalyst, whilst also giving a long-lived catalyst, did not lead to a significant increase in productivity.

The study was then extended to amino-functionalised cross-linked polystyrene beads [Scheme 1(*b*)] as a first step towards controlling the morphology of the resultant polyethylene particles. A mixture of Boc-protected *p*-aminostyrene, styrene and divinylbenzene was polymerised in an equal volume of chlorobenzene in a conventional suspension polymerisation reactor to give solvent expanded highly cross-linked (~12% mol%) spherical beads of fairly uniform diameter (typically 100–150 µm). After deprotection and treatment with CpV(NBu^t)Cl$_2$ under analogous conditions to those described previously, polymerisation at room temperature, this time at 1 atm ethylene pressure, gave a productivity of 10.7 g mmol^{-1} h^{-1}, a figure of merit comparable to the other supported catalysts. Once again steady uptake of ethylene was observed over the 60 min duration of the run.

In summary, the results described here on a model vanadium catalyst system highlight a strategy for covalently attaching transition metal procatalysts to an inert polystyrene support, and importantly demonstrate that dramatically improved kinetic profiles for the polymerisation of ethylene relative to their unsupported analogues can be obtained. There is considerable potential for extending this approach to differently functionalised polystyrenes that will be suited to other classes of transition metal procatalyst, offering the possibility for developing well-defined supports tailored to specific well-defined organometallic procatalysts. The fragmentation of the support will be an important future consideration for controlling the shape and morphology of the growing polyethylene particles.

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Notes and References

† E-mail: V.Gibson@ic.ac.uk

‡ δ_H 0.05 (SiMe$_3$). 1.38 (–CH_2–CHAr–), 1.46 (–CH_2–CHPh–), 1.68 (–CHPh–), 1.80 (–CHAr–), 6.5–7.1 (aryl H); M_w 76700, M_n 51400, M_w/M_n 1.49. 6.3% bis(trimethylsilyl)aminostyrene copolymer.

§ This figure is a conservative value calculated on the assumption that all of the vanadium in solution is transferred onto the solid support and that all of the supported procatalyst is successfully injected into the reactor.

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