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Polymer-supported metal complex alkene epoxidation catalysts

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Abstract

Following a brief background description of homogeneous alkene epoxidation catalysts and early attempts to immobilise these, the most recent developments in the supporting of these species are reviewed. The area is divided into non-chiral and chiral catalysts. Within the former the key combinations that are described are the Mo(VI) and V(V)/alkyl hydroperoxide systems, upon which a great deal of structural evaluation has also been carried out, and W(VI)/H_2O_2. A brief summary of results using immobilised Cu, Mn, Fe, Ru and Ti with alkyl hydroperoxide is also given. In the case of chiral catalysts the main systems described are those mimicking the Sharpless tartrate ester/Ti(IV)/hydroperoxide system for epoxidation of allylic and related alcohols, and those related to Jacobsen's chiral Mn(III) (salen) system for epoxidation of internal non-functionalised *cis*-alkenes. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Polymer support; Epoxidation; Non-chiral catalysts; Chiral catalysts; Alkyl hydroperoxide system

1. Background

Epoxides represent a very important group of speciality and fine chemicals because they are derived directly from alkenes, a primary petrochemical source, and because of the breadth of opportunity they offer the organic synthetic chemist in terms of the highly selective reactions they undergo, often requiring only very mild conditions. Since most epoxides also bear at least one stereogenic centre the strategic importance of these molecules in synthesis is even higher.

In principle it would be nice if all epoxides could be formed from corresponding alkenes by oxidation with molecular O_2 or air, possibly in the presence of a catalyst. Generally, however, it has so far proved impossible to do this with high conversion and high selectivity, except in the case of ethene, where ethylene oxide is produced by direct oxidation with O_2 using e.g. an alumina supported silver catalyst [1]. Higher alkenes are usually more reactive towards O_2 at the allylic carbon position whether in an auto-oxidation or a metal catalysed oxidation reaction [2]. In order to improve selectivity towards epoxidation of the C=C bond it is necessary to use some other oxygen source such as H_2O_2, ROOH, RCO_3H, NaOCl, $KHSO_5$, $NaIO_4$ or PhIO, so-called single oxygen donors [3]. These often function via a metal complex catalysed heterolytic fission mechanism such that free radical species are not involved, and allylic oxidation of the alkene is avoided. In the case of peroxy acids direct stoichiometric epoxidation can occur without activation by a metal complex catalyst. However, the most cost effective of these species are H_2O_2, ROOH and NaOCl, although the latter can give rise to drawbacks involving chlorinated by-products.

The metal complexes most useful as alkene epoxidation catalysts are those based on Ti(IV), V(V), Mo(VI) and W(VI) [4], although recently methyltroxo-rhenium (MTO) has attracted significant attention in this context [5]. Mn(III) salen complexes

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have also assumed considerable importance recently as asymmetric epoxidation catalysts [6]. In terms of polymer-supported systems the most widely investigated are V(V)/ROOH; Mo(VI)/ROOH; W(VI)/H_2O_2; Ti(IV)/ROOH and Mn(III)/RCO_3H.

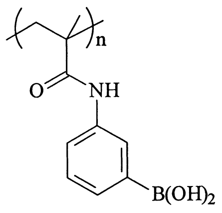
The potential technological advantages in converting a process catalysed by a homogeneous metal complex into one involving a heterogeneous polymer-supported analogue have been well rehearsed [7–10]. Suffice to say that on a laboratory scale supported metal complex catalysts considerably facilitate product work-up and isolation, while on a large scale such heterogeneous species allow processes to be run continuously using packed or fluidised bed columns with considerable financial advantages both in terms of capital expenditure on plant and with regard to recurrent costs. The problems arising with polymer-supported catalysts have also been highlighted [11] and need always be borne in mind.

1.1. Early polymer-supported metal complex catalysts

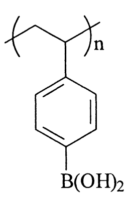
A wide variety of homogeneous metal complex catalysts have been immobilised on polymers [7,8] ranging from alkene hydrogenation, hydroformylation, hydrosilylation, isomerisation and polymerisation catalysts to a growing number of alkene oxidation catalysts. The latter were reviewed in 1988 [12]. In the case of alkene epoxidation catalysts early investigators used sulfonic acid type cation exchange resins [13], carboxylic acid cation exchange resins [14], anion exchange resins [15] and specifically tailored chelating ion exchange resin [16–20] as the polymer support. The nature of the polymer was generally not regarded as being too important in these first studies, with the main aim simply to devise heterogeneous analogues of homogeneous catalysts that displayed some catalytic activity and selectivity.

1.2. Polymer-supported Mo(VI) and V(V) alkyl hydroperoxide systems

More recent studies of supported Mo(VI) and V(V) hydroperoxide alkene epoxidation studies have been reported by Tempesti et al. [21], Stamenova et al. [22] and indeed our own research group, initiated in the latter case by work completed by Simpson [23]. The Italian group [21] employed two boronic acid group-containing resins (**1**) and (**2**), reporting immobilisation of Mo(VI) via reaction 1.



(**1**)



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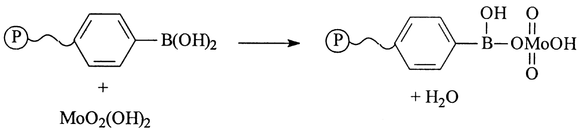
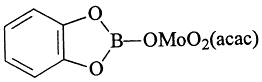


Reaction 1

There was spectral evidence for formation of B–O–Mo bonds, and when the heterogeneous B(III)–Mo(VI) bimetallic species was employed in liquid phase epoxidation of cyclohexene using *t*-butyl hydroperoxide (TBHP) or ethylbenzene hydroperoxide (EBHP) as the oxidant, catalytic activity and selectivity comparable to the homogeneous bimetallic species (**3**) and (**4**) were observed.



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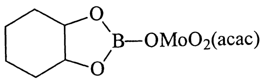


(**4**)

In contrast, the Bulgarian group [22] employed rather ill-defined ethylene-propylene rubber and cross-linked poly(ethylene oxide) grafted or interpenetrated with poly(acrylic acid), poly(methacrylic acid), poly(4-vinyl pyridine) and poly(vinyl alcohol) as the polymer support. Mo(VI) and V(V) were immobilised in some ill-defined manner, and the heterogeneous catalysts were found to be active in styrene epoxidation using EBHP as the oxidant.

Our own first attempts [23,24] with in-house carefully designed and synthesised polymer supported species involved the chelating resins shown in Fig. 1. Immobilised Mo(VI) proved to be very active and selective and more so than the analogous V(V) species in the liquid phase epoxidation of cyclohexene using *t*-butylhydroperoxide as the mono-oxygen

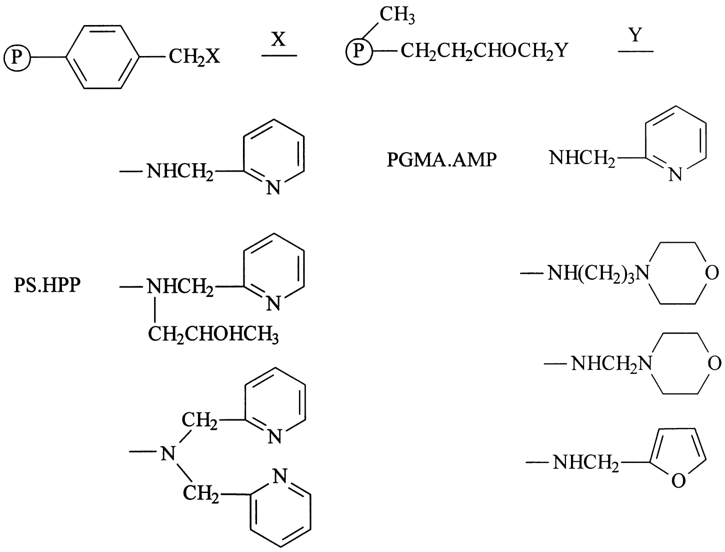


Fig. 1. Structures of poly(chloromethylstyrene)-based (PCMS) and poly(glycidyl-methacrylate)-based (PGMA) chelating resins for Mo(VI) immobilisation [24].

source. Reactions were run under conditions of excess alkene relative to oxidant to maximise selectivity. Unfortunately, all the polymeric catalysts displayed a significant induction period, which could, however, be eliminated by pre-oxidising the catalyst with the hydroperoxide prior to a catalytic reaction. Perhaps a more important negative, however, again characteristic of all the resins studied, was the tendency to leach Mo(VI) during repeated use, although some of the polymers did show evidence of stabilisation with ageing. A crude measure for the likely technological potential of polymeric ligands in oxidation reactions is afforded by their behaviour in thermogravimetric analysis (TGA). Data for the polymethacrylate based resin, PGMA.AMP, and its Mo(VI) complex in oxygen show that at ~200°C both the non-loaded and Mo(VI)-loaded resins start to undergo rapid oxidative decay with progressive loss of mass [25]. Polystyrene-based systems display similar instability.

We reported the use of a very thermo-oxidatively stable porous resin, polybenzimidazole (PBI) as a support for Mo(VI) (PBI.Mo) in the epoxidation of cyclohexene in 1995 [26]. The polymer catalyst proved to be highly active, but also required no pre-oxidation to generate the active species. Subsequently, a range of imidazole-containing resins were synthesised, loaded with Mo(VI), and shown to be similarly active without any activation step (Fig. 2). Furthermore, the supported catalysts could be recycled in batch with essentially no leaching of Mo (detection limited $<0.2\%$), apart from a small loss (2–5%) in the first use (weakly bound or physically trapped component?). Despite this stability, however, the activity of PBI.MO was found to drop on recycling in cyclohexene epoxidations [27] and while the loss of activity could be reduced by oxidising in hydroperoxide, this treatment seemed simply to delay the deactivation of the catalyst. On the optimistic side, however, TGA data for PBI and PBI.Mo in oxygen showed, as expected, that these species are stable beyond ~400°C and so offer a real prospect for technological application [25], given a maintenance of catalytic activity.

A key industrial process in this context is the production of propylene oxide by direct oxidation of propylene with alkyl hydroperoxides using a soluble Mo(VI) catalyst (Halcon or Arco process) [28]. Although the Shell Company have described a heterogeneous Ti(IV)-silica catalyst [29], the development of an industrial heterogeneous analogue of the Mo(VI)-based system remains a scientific and

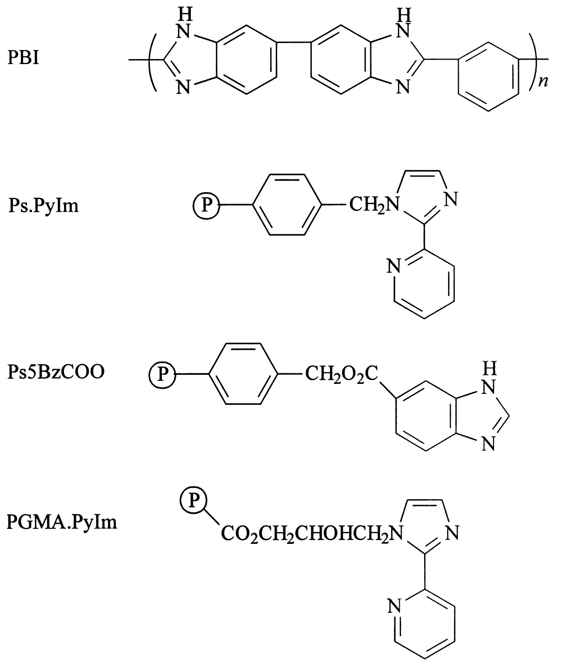


Fig. 2. Imadazole-containing resins for Mo(VI) immobilisation (Ⓟ=vinyl polymer backbone) [25].

technological challenge. Our first epoxidations of propylene using PBI.Mo were in 1994 [25] with a detailed description of the behaviour of a full range of resins following later [30]. Table 1 shows the remarkable ageing behaviour of PBI.Mo over 10 recycles using conditions which represent a realistic technological test along with comparative data for a polystyrene-based species (PsHHP.Mo) and a polymethacrylate-based system PGMA.AMP.Mo. Though under the conditions used the activity of PBI.Mo is the poorest initially, progressive use leads to a very potent and highly selective catalyst. Furthermore, apart from the first catalytic run there is negligible leaching of Mo from PBI.Mo, whereas the other two species, while maintaining reasonable activity over this time scale, show a steady leakage of Mo. The recycling behaviour of PBI.Mo in propylene epoxidation contrasts markedly with its reuse in cyclohexene epoxidation, and this substrate (and potentially product) dependence of recyclability is well known with traditional inorganic-based heterogeneous catalysts. In the latter instance the behaviour is often associated with contamination and physical blocking of the catalyst by side-products, or products arising from subsequent reaction of the main product (e.g. oligomerisation and tar formation). This seems to be the most likely explanation for the deactivation of catalyst in the case of cyclohexene, and the process responsible may well be ring-opening of the product cyclohexene oxide. The contrasting increase in catalytic activity and selectivity in the case of propylene epoxidation most likely arises from microenvironmental changes in the polymer support allowing a

Table 1
Epoxidation of propene using TBHP recycling experiments with catalysts PBI.Mo, Ps.HPP.Mo and PGMA.AMP.Mo [25]

Run	PBI.Mo[a]		PS.HPP.Mo[b]		PGMA.AMP.Mo[b]	
	Yield propylene[c] oxide (%)	Mo leached[d] (%)	Yield proplylene oxide (%)	Mo leached (%)	Yield propylene oxide (%)	Mo leached (%)
1	59.0	2.9	98.7	2.9	84.5	0.7
2	68.4	0	85.5	2.2	82.8	0.7
3	74.8	0	90.1	2.2	94.8	0.7
4	74.1	0	79.9	3.6	88.6	0.7
5	80.4	0	91.3	4.4	96.6	0.7
6	84.6	0	99.0	2.2	93.6	0.7
7	87.4	0	65.2	2.9	99.0	2.1
8	89.7	0	85.9	0.7	83.9	0.7
9	94.8	0	87.0	0.7	82.0	0
10	99.8	0	–	–	81.7	0

[a] Non-activated catalyst.
[b] Catalyst activated for 4 h.
[c] Yield after 1 h based on conversion of TBHP; i.e. 10 mmol TBHP=10 mmol propylene oxide≡100% yield.
[d] Expressed as a % of metal originally loaded on polymer sample. Detection limit indicates <0.2%.

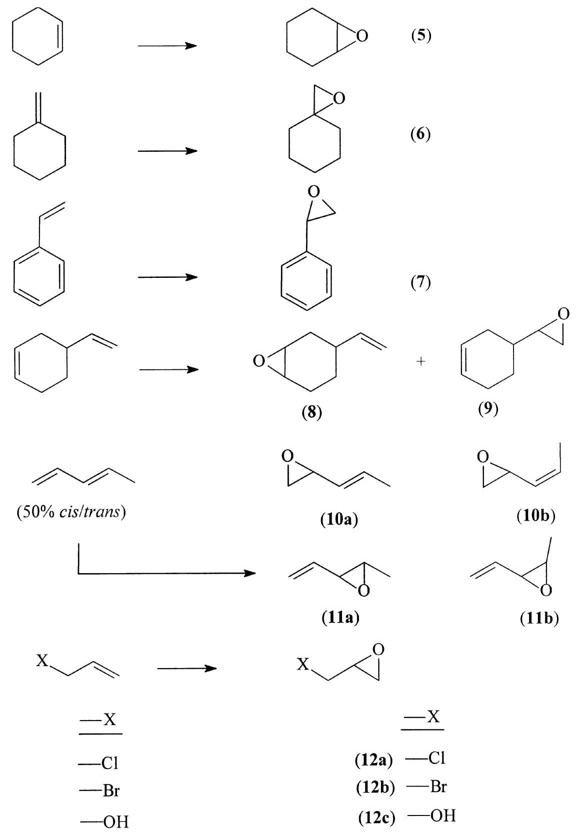


Fig. 3. Epoxidation of alkenes by TBHP catalysed by heterogeneous PBI.Mo [31].

larger percentage of the bound Mo(VI) to become accessible for catalysis.

The PBI.Mo catalyst has also proved to be very useful in epoxidation of a range of alkenes (Fig. 3 and Table 2) [31]. Again all of these reactions were carried out under conditions of excess alkene to maximise selectivity towards epoxide. Rather interestingly, in the course of marking some careful catalyst recycling experiments it was found that if air was not excluded from reactions then over an extended reaction period molecular O_2 becomes involved as an oxidant giving some allylic oxidation products where this is possible (e.g. 2-cyclohexene-1-ol and 2-cyclohexene-1-one from cyclohexene) in addition to the major epoxide product. At the same time, however, yields of epoxide exceed (sometimes considerably, see entry 1, Table 3) that achievable from the quantity of TBHP used in the reaction. This almost certainly arises from in situ generation of cyclohex-2-enyl hydroperoxide via oxidation with O_2, and this additional hydroperoxide is then able to participate in epoxidation of more cyclohexene. This argument is confirmed by model reactions under a blanket of N_2, when no aerobic oxidations can contribute, and under these conditions only clean epoxidation of e.g. cyclohexene is observed. Also, in the case of an alkene, e.g. styrene, which cannot undergo aerobic allylic oxidation, this complication is not observed.

Whilst performing alkene epoxidations under conditions of excess alkene is fine for large-scale processes in which the alkene can be conveniently recycled [32], these are not appropriate for speciality alkenes in small scale (batch) pharmaceutical or agrochemical syntheses, where in economic terms it is usually essential to maximise conversion of often precious alkene precursors. We have recently examined the epoxidation of cyclohexene as a model catalysed by PBI.Mo using an equimolar ratio of alkene and TBHP [33]. With appropriate adjustment to the concentration of components and quantity of catalyst it is possible to minimise oxidation side-reactions and deliver good yields of epoxide (e.g. entry 7, Table 4).

One of the great potentials offered by polybenzimidazole (PBI) as an oxidation catalyst support is its remarkable thermo-oxidative stability. Unfortunately, the resin is rather expensive and this has led us to explore other very stable polymers as potential supports, and particularly ones that might prove less expensive.

The polyimide range of polycondensation species are well developed high performance polymers [34] and display thermo-oxidative stability at least as good as PBI. We have shown with our Korean collaborators that these materials can be synthesised in the form of porous spherical particulates by suspension polycondensation in paraffin oil [35] using traditional chemistry involving a bis-anhydride and bis-aromatic amine. In this instance the precursors are less expensive then those used to prepare PBI and so in principle supports based on these species are likely to be more cost effective than PBI. By using a functional bis-amine we have also been able to synthesise polyimide particulates containing ligands and other exploitable functional groups [36] and some of these prove capable of binding Mo(VI). Thus a polyimide species with a 1,2,4-triazole unit in the backbone (**13**)

Table 2
Epoxidation of alkenes by *t*-butylhydroperoxide catalysed by PBI.Mo [31]

Alkene	PBI.Mo (mmol Mo)	Temperature (°C)	Product	Maximum conversion (%); Time (min)	TOF[a] mol prod.(mol per Mo min^{-1})
Cyclohexene	0.038	60	(**5**)	105 (400)	1.36
Methylenecyclohexane	0.038	60	(**6**)	99 (400)	0.70
Styrene	0.038	60	(**7**)	95 (700)	0.38
4-Vinylcylcohexene	0.038	60	(**8**)	87 (2000)	0.41
			(**9**)	15 (2000)	0.17
			Dioxide	∼0	∼0
1,3-Pentadienes (50% *cis*/*trans*)	0.038	60	(**10a**)	∼6 (300)	∼0.3
			(**10b**)	∼8 (300)	0.10
			(**11a**)	10 (300)	0.21
			(**11b**)	11 (300)	0.24
Allyl chloride	0.10	45	(**12a**)	30 (400)	0.06[b]
Allyl bromide	0.10	45	(**12b**)	∼6 (400)	<0.01[b]
Allyl alcohol	0.10	45	(**12c**)	∼5 (400)	<0.01[b]

[a] At a time of ∼50% conversion.

[b] At a time of 20% maximum conversion.

Table 3
Recycling of PBI.Mo catalyst and effect of added 3,5-di-*t*-butyl catechol and N_2 atmosphere[a] [31]

Alkene/conditions	Run	Epoxide (%)	Other products (%)	
Cyclohexene		(**5**)	2-Cyclohexene-1-ol	2-Cyclohexene-1-one
Air	1	168	94	23
	2	94	114	48
	3	6	7	11
Catechol	1	43	0	0
N_2	1	102	0	0
	2	76	0.5	0
Styrene		(**7**)		
Air	1	91	0[c]	0[c]
	2	103	0[c]	0[c]
	3	111	0[c]	0[c]
4-Vinylcyclohexene		(**8**)	(**9**)	Allylic oxidation
Air	1	63	5	CNQ[b]
	2	22	4	CNQ
	3	14	5	CNQ
Catechol	1	37	0	0
N_2	1	61	0	0
	2	62	0	0
1,3-Pentadiene		All monoepoxides[d]		
Air	1	21		
	2	56		
	3	53		

[a] 60°C for 24 h.

[b] CNQ: complex and not quantified.

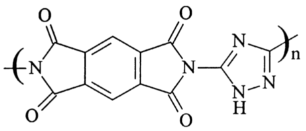
[c] No other products seen.

[d] Total yield sum of all epoxides.

Table 4
Epoxidation under equimolar conditions of cyclohexene/TBHP catalysed by PBI.Mo [33]

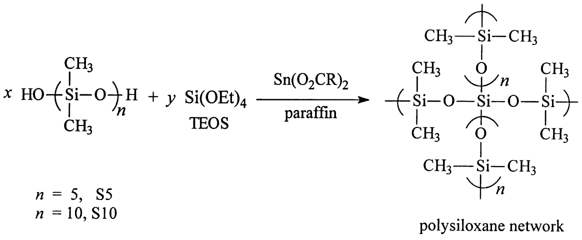
Run	PBI.Mo (mmol, mol%)	TBHP[g] (ml, mmol)	Cyclohexene (ml, mmol)	Toluene (ml)	Temperature (°C)	Epoxide yield (%) (24 h)
1	0.06, 1.2	1.5, 5.2	0.53, 5.2	7.0	80	∼35
2	0.06, 0.3	5.8, 20	2.0, 20	1.2	80	50
3	0.2, 1.0	5.8, 20	2.0, 20	1.2	80	50
4	0.06, 0.3	5.8, 20	2.0, 20	1.2	60	∼25
5	0.2, 1.0	5.8, 20	2.0, 20	1.2	60	∼25
6	0.06, 0.3	5.8, 20	2.0, 20	1.2	60	∼25
7	1.0, 5.0	5.8, 20	2.0, 20	1.2	80	70
8	0.06, 1.2	1.5, 5.2	7.5, 73	–	80	100 (3 h)
9	0.06, 0.4	8.0, 28	1.4, 14	–	80	38
10	2.0, 5.0	11.6, 40	4.1, 40	2.3	80	50
11	1.0, 5.0	5.8, 20	2.0, 20	1.2	80	65

not only binds Mo(VI) but is an active catalyst in cyclohexene epoxidation [36]. Interestingly, while a linear resin version of this polymeric ligand yielded a supported Mo(VI) catalyst which showed slow deactivation on recycling in TBHP epoxidation of cyclohexene, a cross-linked version provides a much more stable system and was recycled 10 times in batch without loss of activity [37]; effectively performing better than our PBI.Mo catalyst with this alkene. The technological potential is clear here.



(13)

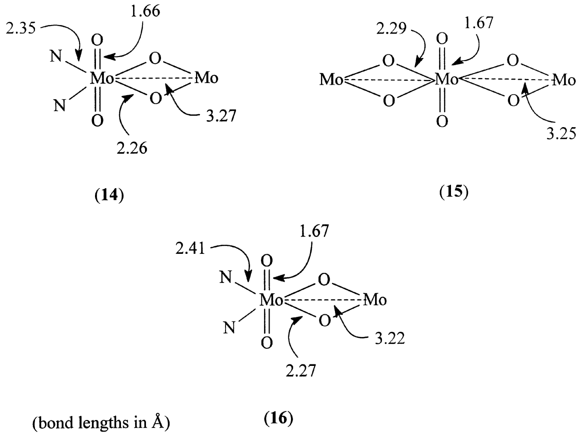
Most recently, our research group has succeeded in synthesising spherical polysiloxane-based resin particles using a dispersion polycondensation technique [38]. Again polysiloxanes are thermo-oxidatively very stable. The chemistry involves the reaction of short silanols with tetraethoxysilane (Reaction 2) and hence allows proportions of the latter to be replaced with functional trialkoxysilanes such as trimethoxysilyl-2-ethylpyridine. The resultant polysiloxane particles carrying their pyridine functionality are able to bind Mo(VI) and are highly active catalysts in cyclohexene epoxidation using TBHP. Indeed, the level activity per Mo centre is far higher than with PBI.Mo and preliminary data shows the level of Mo leaching to be very low. Bearing in mind that polysiloxane-based supports are likely to be significantly less expensive than both polybenzimidazole and polyimide-based systems, the former seem well worthy of further investigation.



Reaction 2

1.3. Structure of polymer-supported Mo(VI) species

Although a number of polymer-supported Mo(VI) species have proved to be very active, selective and stable heterogeneous catalysts for alkene epoxidations using hydroperoxides, characterising the structure of the active catalytic site has proved highly problematical. There is little doubt that the active site must have much of the character proposed by Sharpless et al. [39] and Mimoun [40]. Most progress in developing a full understanding has been made by Tempesti and his collaborators [41], by Imamura et al. [42] in the case of alumina-supported species, and by our own group and our collaborators [43]. There is general agreement that octahedral Mo(VI) species are involved. We have used elemental analysis, FTIR spectroscopy, electronic and X-ray photoelectron (XPS) spectroscopies together with X-ray absorption fine structure



(14) **(15)** **(16)**

(bond lengths in Å)

Fig. 4. Best-fit structures from EXAFS data for ‘average’ Mo centres in PSHPP. ‘As-synthesised’ (**14**); PSHPP.Mo ‘activated’ (**15**); and both PBI.Mo ‘as synthesised’ and ‘activated’ (**16**) [43].

analysis (EXAFS) analysis and associated modelling to develop a comprehensive picture of the evolution of the molecular structure of the active sites, and have also characterised the associated morphological changes using high-resolution transmission electron microscopy (TEM) with Mo mapping, N_2 sorption and Hg intrusion porosimetry, and solvent imbibition measurements. In summary FTIR spectra confirm the presence of Mo=O and Mo–O–Mo in both the PBI resin support (Fig. 2) and in a polystyrene resin bearing a hydroxypropylaminomethyl pyridine ligand, PS.HPP (Fig. 1). XPS data confirm that overwhelmingly Mo is in the +6 oxidation state in both the ‘as-synthesised’ catalysts and in catalysts contacted (‘activated’) with TBHP. Modelling of the EXAFS data yields the best fit structures for ‘average’ Mo centres in ‘as synthesised’ and ‘activated’ polymer catalysts as shown in Fig. 4. The evolution of structures is shown schematically for both polymer supports in Fig. 5, with ‘as-synthesised’, ‘activated/resting’ and ‘actual active’ species defined. In the case of PBI.Mo high resolution Mo mapping in the TEM analysis confirms that the Mo species are very uniformly distributed throughout the resin and are not present as discrete MoO_3 crystallites but as much smaller structures. Morphological differences between PBI and PSHPP also appear to contribute in part to the differences observed in catalytic behaviour [43].

1.4. Polybenzimidazole-supported Cu, Mn, Fe, Ru and Ti hydroperoxide systems

To complement our studies on Mo(VI)-based polymer catalysts we have also examined a number of other metal centres which are likely to offer useful catalytic opportunities. Using cyclohexene as a model substrate and TBHP as the oxidant in the presence and absence of air, Cu, Mn, Fe, Ru and Ti have all been shown to be catalytically active when supported on PBI [44]. The conversion data in Table 5 show that PBI.Cu, PBI.Mn

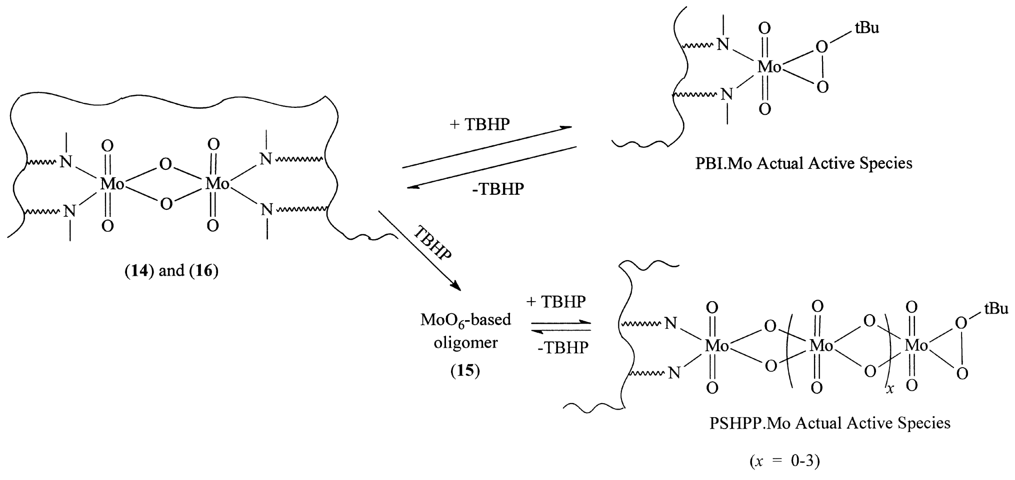


Fig. 5. ‘As-synthesised’, ‘activated/resting’ and ‘actual active’ species in PSHPP.Mo and PBI.Mo [43].

Table 5
Maximum conversions[a] to products from oxidation of cyclohexene by TBHP catalysed by PBI-metal complexes [44]

Catalyst	Maximum conversion (%)					Total (%)	Temperature atmosphere
	Cyclo-hexeneoxide	2-Cyclo-hexene-1-ol	2-Cyclo-hexene-1-one	*t*-Butyl cyclohex-2-enylperoxide	Cyclo-hexane-1,2-diol		
PBI.Cu	7.0	27	220	43	$\sim$0	280	60/air
PBI.Cu	0.88	1.1	6.4	78	$\sim$0	86	60/N_2
PBI.Cu	0.95	1.3	3.2	60	$\sim$0	66	60/N_2
PBI.Mn	5.0	31	100	$\sim$0	$\sim$0	140	60/air
PBI.Fe	20	67	210	64	$\sim$0	370	60/air
PBI.Ru	11	37	60	$\sim$0	90	200	60/air
PBI.Ti	62	47	$\sim$140	$\sim$0	41	220	60/air
PBI.Ti	24	$\sim$0	$\sim$0	$\sim$0	$\sim$0	24	60/N_2
PBI.Ti	73	$\sim$0	$\sim$0	$\sim$0	$\sim$0	730	80/N_2

[a] Data based on 5 mmol TBHP oxidant. Values >100% confirm involvement of O_2 as an oxidant.

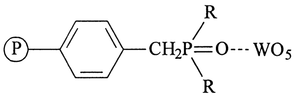
and PBI.Fe are all potentially useful allylic oxidation catalysts, PBI.Ru offers an opportunity in dihydroxylation, and perhaps not surprisingly, PBI.Ti shows significant selectivity towards epoxidation. In the absence of O_2, cyclohexene oxide is the sole product in the case of PBI.Ti. The various selectivities have been rationalised in the light of the known behaviour of these various metals [44].

1.5. Polymer-supported W(VI) H_2O_2 systems

Alkyl hydroperoxides are very useful mono-oxygen sources, are very safe, requiring a metal complex to activate them, and are of reasonably low cost. However, these oxidants are not readily available at all world-wide petrochemical sites and do yield an alcohol co-product that must either be used in-house or sold externally to balance the economics of using hydroperoxides. In principle H_2O_2 has more potential since it is more widely available, is cheaper, and increasingly importantly is much cleaner, yielding only H_2O as a co-product. H_2O_2 is readily activated by W(VI) to yield a potent and selective alkene epoxidation system [45]. In this context W(VI) complexes are much better than Mo(VI) and V(V) species. Ideally dilute aqueous H_2O_2 (35%) is the favoured oxidant since it is cheaper and safer than the more concentrated forms typically available (50, 70 and ~100%). However, the presence of H_2O can give rise to alkene dihydroxylation concurrently with epoxidation.

The problem in designing and producing polymer-supported analogues of W(VI) catalysts is that in homogeneous reactions W(VI) is most conveniently available, and indeed exploited, as a complex oxyanion e.g. $W_2O_{11}^{2-}$ or WO_4^{2-}. While facile and direct immobilisation of these on an anion exchange resin is possible, use in aqueous solutions also offers potentially facile leaching of the catalyst also by anion exchange.

Early work on these systems was reported by Allan and Neogi [46], Kalal and co-workers [47] and more recently by Kamatudin and Singh [48]. However, Gelbard and his group have made perhaps the major contribution [49]. They have employed a range of macroporous and gel-type poly(methacrylate)-based quaternary ammonium resins to immobilise HWO_5^- and achieved good catalytic turnover in the epoxidation of cyclohexene using 70% aqueous H_2O_2. Selectivity towards epoxide was, however, only modest (22–68%). Immobilisation of W(VI) species on pyridinium ion, and pyridine-*N*-oxide containing polystyrene resins gave similar results. Since Gelbared et al. had already shown that homogeneous W(VI) complexes with organophosphorus ligands containing the phosphoryl unit $\geqslant\mathrm{P{=}O}$ (e.g. hexamethylphosphotriamide, HMPA, and trioctyl-phosphine oxide, TOPO) gave much improved performance in the H_2O_2 epoxidation of simple alkenes and allylic alcohols [50], they synthesised a number of polystyrene supports with phosphine oxide and phosphonamide functionality as well as a polybenzimidazole resin with phosphonamide groups. Each of these was loaded with W(VI) using peroxotungstic acid, $H_2W_2O_{22}$. The phosphine oxide-containing resin catalyst (**17**) gave similar or better catalytic turnover than a soluble model complex with cyclohexene and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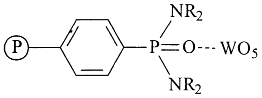
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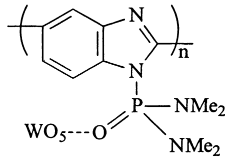
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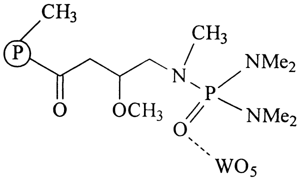
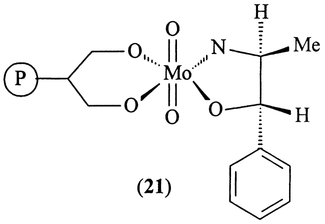

(**20**)

H_2O_2 (70%). However, the supported complex was too unstable to allow recycling. The corresponding polystyrenephosphonamide-derived catalysts (**18**) were similarly active and some were successfully recycled two and some three times. The polybenzimidazole species with phosphonamide ligands (**19**), though somewhat less active, seemed perfectly stable and was reused five times without loss of activity or attenuation of selectivity. The leakage of W was also below the threshold limit of detection (<2 ppm). In a very detailed back-up study Gelbard et al. have shown a tailored polymethacrylate resin carrying phosphonamide ligands to yield a W(VI) catalyst (**20**), with very high selectivity towards epoxidation of cyclohexene using 65% aqueous H_2O_2 [51]. The levels of diol produced, and allylic oxidation by-products are very low and the overall selectivity towards epoxidation far higher than achieved with a soluble model complex catalyst.

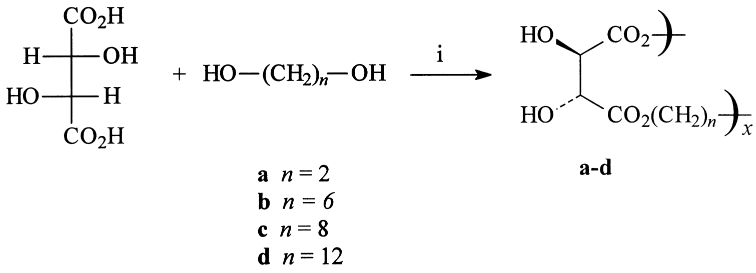
1.6. Polymer-supported asymmetric Ti catalysts in allylic alcohol and related epoxidations

A very important organic synthetic methodology both in the research laboratory and in a number of industrial processes is the use of the Sharpless Ti-tartrate ester-based asymmetric alkene epoxidation system [52]. Typically in the catalytic form [53] 5–10% mol $Ti(O^iPr)_4$ complexed with dimethyl or diethyltartrate in CH_2Cl_2 converts allylic alcohols in 70–90% yield to corresponding epoxide with an enantioselectivity of >90% enantiomeric excess (ee). Exchanging the D-(−)-tartrate ester for the L-(+)-tartrate allows both enantiomers to be synthesised equally effectively. Somewhat surprisingly there has been relatively little effort made to produce polymer-supported analogues of this system and one reason may be the relatively low cost of tartaric acid diesters which tolerates their loss during work-up. However, it turns out that in some instances, for example, with water soluble substrates, the standard work-up procedure for the soluble catalyst system presents major problems, so much so that these preclude convenient and cost-effective use of the methodology. Under these circumstances a polymer-supported system would be invaluable, and indeed might then be exploited more widely as a more practical methodology.

Before our own work was initiated on the Sharpless system we were aware of only one report on the synthesis and evaluation of a polymer-supported analogue [54]. In 1983 Farrall and co-workers immobilised a single tartrate residue on a 1% cross-linked polystyrene resin and performed Sharpless epoxidation of geraniol under literature conditions. Typically yields of the desired product were 60–70% and enantiomeric excess 50–60%. The polymer ligand was also reported to be recyclable. In retrospect this was a very good result and it is surprising the work was not followed up earlier. Interestingly, Cazaux and Caze reported their results on the immobilisation of an asymmetric Mo(VI) complex (**21**) in 1993 [55]; and again they employed this to catalyse epoxidation ofgeraniol. Their results were poorer and the polymer catalyst was reported to be unstable. That the chiral polymer Mo(VI) complex was less effective is not surprising since low molecular weight soluble complexes of Mo(VI) of similar structure are also less selective than the Ti-tartrate complex [56].


(**21**)

In collaboration with Finnish colleagues our own group reported the synthesis of a range of linear polytartrate esters in 1997 [57] where the optically active ligand is a component of the polymer backbone (Fig.



(**22**)

Fig. 6. Synthesis of linear poly(tartrate ester)s for use in Sharpless epoxidations.

6). The objective was to combine the role of the polymer support and the active functionality attached to the support in order to maximise weight effectiveness and minimise possible mass transfer problems within the support. Use of these polytartrates with $Ti(O^{i}Pr)_4$ and TBHP under typical Sharpless conditions gave good yields of epoxide from *trans*-hex-2-en-1-ol with ee% up to 80%. Perhaps equally importantly there is a strong 'polymer effect'. Polytartrate (**22a**) gave essentially a racemic product. This ligand and its Ti complex are essentially insoluble in the reaction medium. Solubility improves with (**22b**), while the Ti complex of (**22c**) is completely soluble and the reaction essentially homogeneous. This species gave the highest ee% and led us to prepare (**22d**) which itself, along with its Ti complex, are soluble in CH_2Cl_2. In the event no further improvement in ee% was observed with this ligand.

With the above result in hand the synthesis of (**22c**) was repeated to provide more polymeric ligand for use with more substrates. In the course of producing further batches it was discovered that using slightly more forcing preparation conditions it was possible to produce branched poly(tartrate ester)s (**22e**) and even cross-linked species (Fig. 7), the degree of branching being evaluated from ^1H NMR spectra (400 MHz) [58]. Somewhat to our surprise polymers with a degree of branching ≤15% were totally soluble in DMSO, but formed insoluble Ti complexes under conditions of the Sharpless reaction. Furthermore, these heterogeneous polymer catalysts gave higher levels of induction in epoxidation of *trans*-allylic alcohols [58] (Fig. 8, Table 6) than the soluble linear analogues used earlier. In addition, since the catalysts are heterogeneous, work-up of the reaction is considerably facilitated. A recent report of this work [59] played down the significance of these results since the authors would have been unaware of the data from the branched polytartrates. Contrary to the above commentary the high level of activity and selectivity displayed by appropriate heterogeneous poly(tartrate ester)s do offer technological potential, especially in the cases where work-up of products has proved so difficult as to nullify the advantage of using the Sharpless methodology.

Somewhat intriguingly polymers which are fully cross-linked and hence insoluble even in DMSO, and for which solution phase ^1H NMR data cannot be obtained, gave disappointingly low levels of enantios-

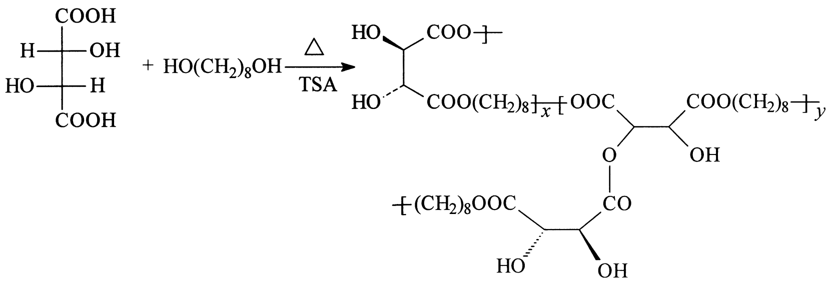


Fig. 7. Synthesis of branched poly(octamethylene-L-(+)-tartrate) [58].

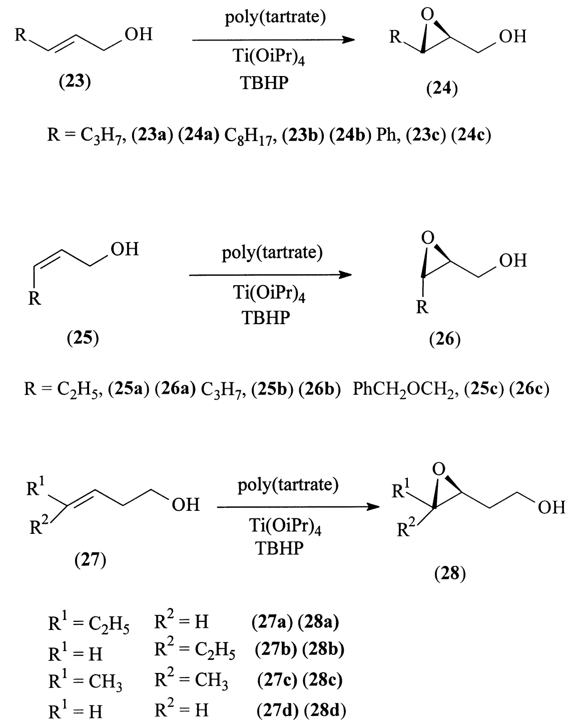


Fig. 8. Sharpless epoxidation of *cis*- and *trans*-allylic and homoallylic alcohols catalysed by poly(tartrate ester) (**22e**) [58,60,61].

electivity in epoxidations [58]. Why this should be so is not clear. It may be that the fully cross-linked polymers inhibit formation of a high proportion of the specific Ti complex required to provide high levels of asymmetric induction. It may also be that mass transfer limitations disturb the balance of reaction steps.

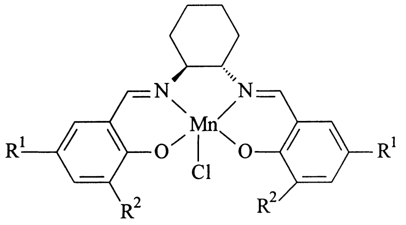
The potential importance of these poly(tartrate ester) ligands becomes more apparent on widening the alkene substrates investigated. Generally dialkyltartrate esters provide lower levels of enantiocontrol in epoxidation of *cis*-allylic alcohols than they do with the *trans*-isomers. The poly(tartrate ester) (**22e**) shows consistently higher ee% than the simple alkyl esters [60] (Fig. 8, Table 6). Perhaps even more surprisingly, whereas the Sharpless methodology is of almost no practical value in the case of homoallylic alcohols, poly(tartrate ester) (**22e**) offers levels of ee% which could be of real value for some of the substrates [61] (Fig. 8, Table 6). Why the polymer ligand should offer this more remote enantiocontrol is not clear, but there may well be an important message here for those interested in developing novel optically active ligands and complexes.

1.7. Polymer-supported chiral Mn(III) (salen) catalysts in alkene epoxidations

The discovery by Jacobsen and his co-workers that C-2 symmetric Mn(III) (salen) complexes (**29**) will function as highly active and enantioselective alkene epoxidation catalysts [62,63], has provided an important new methodology for synthesis of optically active epoxides. Though often quoted as 'useful for non-functional alkenes' in fact, the catalytic system seems optimal for *cis* internal alkenes, and particularly so for cyclic systems. An enormous number of variants of the chiral salen ligand have been described and used as the Mn(III) complex in asymmetric alkene epoxidations. There has also been an intense study world-wide of the mechanism of the reaction, and all aspects of this have been reviewed recently in a scholarly work by Gilheany and his co-workers [6]. The

Table 6
Asymmetric epoxidation of *cis*- and *trans*-allylic and homoallylic alcohols using poly(octamethylene tartrate) (**22e**) $Ti(OiPr)_4$/TBHP [58,60,61]

Alkene	Epoxide	Poly(tartrate) % branching	Molar ratio alkene:Ti:tartrate	Temperature (°C)	Time	Isolated yield (%)	Ee (%)
(**23a**)	(**24a**)	3	10:25:5	−20	6 h	53	87
(**23b**)	(**24b**)	6	10:2:6	−15	12 h	40	98
(**23c**)	(**24c**)	6	10:25:5	−20	6.5 h	38	89
(**25a**)	(**26a**)	10	10:10:20	−20	7 days	51	86
(**25b**)	(**26b**)	10	10:10:40	−20	6 days	48	80
(**25c**)	(**26c**)	10	10:20:40	−20	6 days	18	68
(**27a**)	(**28a**)	8	10:20:40	−20	5 days	45	54
(**27b**)	(**28b**)	10	10:20:40	−20	21 days	20	51
(**27c**)	(**28c**)	3	10:10:20	−20	1 day	31	36
(**27d**)	(**28d**)	10	10:20:40	−20	14 days	20	80



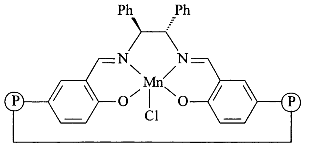
(**29**)

favoured soluble complex (**29**) $R^1=R^2={}^t$Bu–) is relatively costly, rather unstable in contact with oxidant, must be used in a careful experimental protocol and cannot be recycled. The system is, however, versatile in terms of the mono-oxygen source that can be used (e.g. PhIO, NaOCl and $ArCO_3H$).

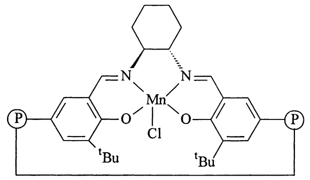
Not surprisingly, there have been a number of attempts to develop highly active and enantioselective polymer-supported analogues of Jacobsen's catalyst [64–70].

As it turns out it is extremely difficult to prepare salen ligands which are non-symmetric in terms of the substituents on the two benzene rings. This is because monocondensation of a diamine with a salicylaldehyde to yield an amino derivatised Schiff base is almost impossible and inevitably almost irrespectively of how the reaction is performed the second amino group undergoes fast condensation as well, to yield the bis-Schiff base i.e. the salen structure. Early attempts to produce a polymer-supported analogue of Jacobsen's catalyst focussed on synthesising styryl derivatives of the chiral salen ligand, and inevitably this led to di-styryl monomers [65–69]. Polymerisation of these, therefore, led to cross-linked polymers in which it would be expected that the salen ligand would be located on cross-links (**30a**–**d**).A great deal of careful evaluation was performed by both an Italian and an Indian group using a number of alkenes, various reaction conditions and a number of oxidants. Overall the results proved rather disappointing. Although some of the supported systems displayed good activity, the level of enantiocontrol was low with the best ee% recorded being ~60% [68,69]. Interestingly, both groups did suggest that recovery and recycling of their polymers was possible, though there was no data given.

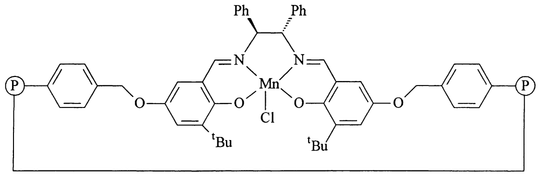
In tackling immobilisation of this catalyst ourselves we were conscious of the mechanistic proposals in the literature all of which implied that local mobility of the complex should not be impaired. Locating the complex on a polymer cross-link would be expected to do just this! Accordingly, we set out with a number of design criteria as follows: (i) the local molecular structure of the Mn complex should mimic precisely the optimum structure of Jacobsen's catalyst (i.e. (**29**), $R^1=R^2={}^t$Bu–); (ii) the complex should be attached by a single flexible linkage to the polymer support to minimise any local steric restriction; (iii) the catalyst should be attached to the polymer with sufficiently low loading to maximise site isolation of catalytic centres, hence minimising the possibility of inactive oxo-bridged dimer formation; and (iv) the morphology of the support should be such that no mass transfer limitation arises, with all active sites freely accessible. In our view the oxidant, *m*-chloroperbenzoic acid with



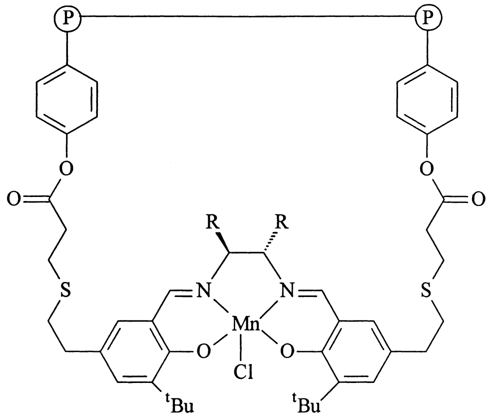
(**30a**)



(**30b**)



(**30c**)



(**30d**)

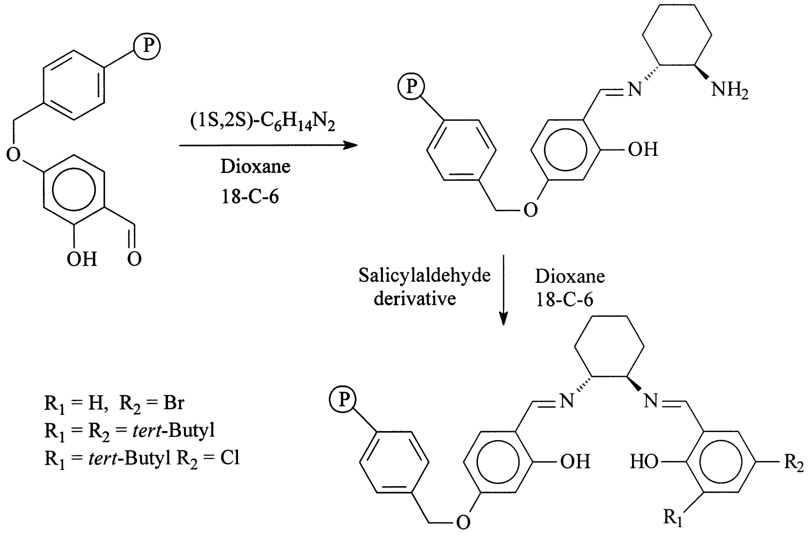


Fig. 9. Synthesis of sited isolated chiral salen complexes supported on resin derived from styryl salicylaldehyde [71].

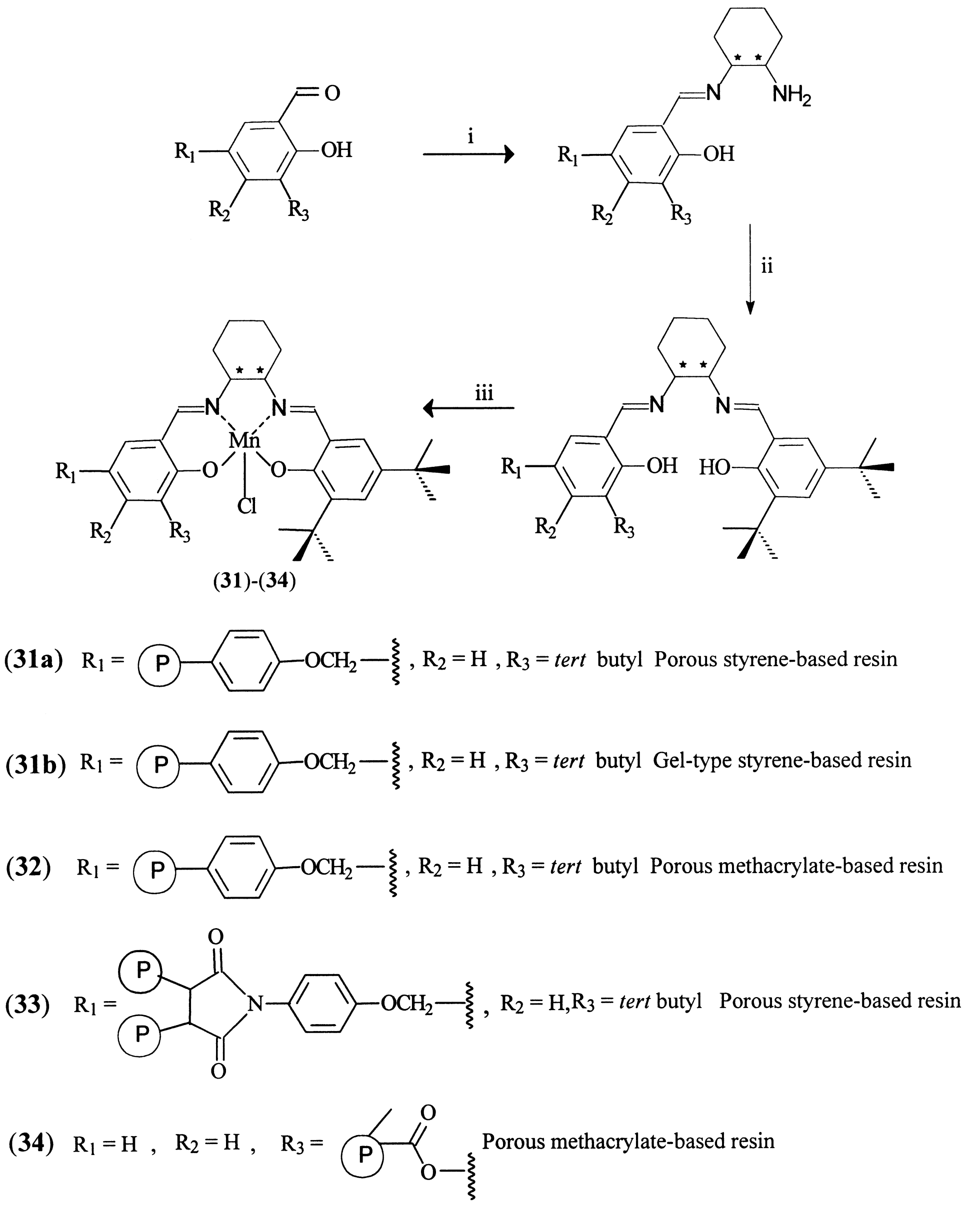
the co-oxidant *N*-morpholine *N*-oxide appeared to be the most productive reported in the literature and we opted to use this oxidation system.

Our strategy to ensure mono-attachment of the salen ligand to the matrix was to build the ligand on the polymer with a loading level such that a large proportion of site-isolation would be achieved. In this way the mono-condensation of the enantiomerically pure *trans*-1,2-diaminocyclohexane with the first matrix-bound salicylaldehyde residue would be assured, allowing the second condensation to be achieved with e.g. di-*t*-butylsalicylaldehyde. Our first synthesis (Fig. 9) involved suspension polymerised resin beads derived from 4-(4-vinylbenzyloxy) salicylaldehyde and the accumulated analytical data suggested that the scheme had worked well [71]. Very disappointingly, both gel-type and macroporous versions of this polymer ligand performed very poorly in asymmetric epoxidations of both indene and 3,4-dihydronaphthalene. The macroporous species were reasonably catalytically active but displayed only low enantiocontrol; the gel-type species displayed both low activity and very poor selectivity. Crucially the first synthetic strategy produced a chiral polymer ligand with one missing *ortho*-*t*-butyl group and so accordingly a second group of resins were synthesised ensuring all the criteria listed above were met [72]. The route adopted is shown in Fig. 10. The catalysts were evaluated in asymmetric epoxidations of a number of *cis*-internal alkenes and the results for 1-phenylcyclohex-2-ene are shown in Table 7. Only the species (**33**) and (**34**) performed poorly. In the case of (**33**) this is probably due to the rigidity of the maleimide copolymer from which it is derived. With (**34**) the link to the polymer is via the C-atom *ortho* to one of the phenol OH groups and clearly this is too sterically crowded. The results with (**31a, b**) and (**32**) are, however, very rewarding and represent the most active and enantioselective of polymer-supported systems reported to date. Structure (**32**), in particular, performs as well as does the soluble Jacobsen model.

In practice, however, we have also observed a strong substrate dependence in the performance of our resins and indeed the soluble catalyst itself is very variable in its performance in our hands. We have succeeded

Table 7
Asymmetric epoxidation of 1-phenylcyclohex-2-ene using MCPBA catalysed by polymer-supported chiral Mn(III) (salen) complex [72]

Catalyst	Configuration	Epoxide		
		Yield (%)	Ee (%)	Configuration
Jacobsen	S,S	72	92	(+)-(R,R)
(**31a**)	R,R	36	61	(−)-(S,S)
(**31b**)	R,R	47	66	(−)-(S,S)
(**32**)	R,R	49	91	(−)-(S,S)
(**33**)	R,R	5	5	(−)-(S,S)
(**34**)	R,R	5	∼0	(−)-(S,S)



Reagents and conditions: i, (*R*,*R*)-1,2-diaminocyclohexane, CH_2Cl_2, room temp., 12 h; ii, 2,4-di-*tert*-butylsalicylaldehyde; iii, CH_2Cl_2, room temp., 12 h; vi, $Mn(OAc)_2.4H_2O$, EtOH, air, reflux, 30 h then LiCl.

Fig. 10. Synthesis of site isolated salen complexes supported on styrene and methacrylate ester-based resins [72].

in recycling the polymeric ligands, both without and with reloading of Mn. In all cases we see a decline in catalytic activity and selectivity, and for the time being at least our view is that the catalyst itself is too fragile for all of it to survive work-up. The latter is, however, considerably simplified with the polymer-supported system and this is a major advantage. In due course full details will emerge from our laboratory [73].

An alternative strategy for the immobilisation of Jacobsen's catalyst would be to avoid attachment via the benzene rings altogether. A simplistic attempt to achieve this has been reported [70] by binding pre-formed Mn complex to a pyridine-containing polystyrene-based resin whereby the pyridine co-ordinates axially to the Mn centre. Since there is strong evidence that both axial positions can become involved in the various catalytic steps arising from Jacobsen-type complexes, axially co-ordinated complexes would be expected either to have low activity, or to become highly mobile during the catalytic cycle and be subject to facile leaching. The claim for such species to be reused with constant activity over 10 cycles, therefore, does appear rather incredulous! The strategy of attachment other than via the salicylaldehyde residues does, however, remain a good one, and synthesis of enantiomerically pure diamines with a functional handle convenient for binding to a resin or other support looks an attractive option.

Another potentially very attractive strategy avoiding the need to synthesise special functional ligands and allowing direct exploitation of commercially available optically pure ligand is to trap the Mn complex physically within a suitable polymer matrix. Attempts to do this in the past with other catalysts have simply led to rapid leaching. However, Vankelecom and his co-workers [74] have reported that physical entrapment of Jacobsen's catalyst in a poly(dimethylsiloxane)membrane provides an active and enantioselective heterogeneous catalyst which compares favourably with the soluble analogue.

Regeneration of the catalyst is also reported. The same group have also synthesised a dimeric form of the catalyst linked by the *para* positions of the benzene rings and reported improved retention of the complex within the polysiloxane membrane [75]. Further details are required to fully evaluate these reports but the prospects are intriguing.

1.8. Immobilisation of chiral Mn(III) (salen) catalysts in inorganic supports

Use of inorganic supports to heterogenise homogeneous metal complex catalysts is in principle as attractive as employing polymer supports and this area has been reviewed recently [76]. Not surprisingly, there have been a number of reports describing the heterogenisation of chiral Mn (salen) complexes using this approach. Sabater et al. have synthesised a chiral Mn(III) (salen) complex within the supercages of zeolite Y [77] (so-called 'ship-in-a-bottle' approach) and have demonstrated similar catalytic activity to the corresponding soluble complex. Ogunwumi and Bein have used a similar strategy in the case of zeolite EMT [78]. Their heterogeneous catalysts produced high enantiomeric excess in the epoxidation of aromatic alkenes with NaOCl. Frunza et al. [79] and Kim and Kim [80] have both used the mesoporous species MCM-41 to immobilise chiral Mn (salen) complexes. In the latter work the Mn complex was introduced into MCM-41 in two ways. First the PF_6^- Mn^+(III) (salen) complexes were exchanged with Na^+ counterion on MCM-41. Secondly, Mn^{2+} was exchanged with Na^+ counterion on MCM-41 and then the bound Mn^{2+} co-ordinated with the chiral salen ligands, oxidised with air, and converted to the PF_6^- salt. The epoxidations of styrene and α-methylstyrene with *m*-chloroperbenzoic acid and *N*-methylmorpholine *N*-oxide were then studied. In general, the heterogeneous catalysts were a little less active than the homogeneous models, but the difference was not significant in terms of synthetic need of epoxidation of unsubstituted terminal alkenes under conditions when the soluble Jacobsen-type catalysts perform rather poorly bodes well for the development and exploitation of heterogeneous catalysts in this area.

2. Where to from here?

During the 1970s through the 1980s and as late as the early 1990s those research groups studying polymer-supported catalysts were regarded with some incredulity by their colleagues focussing on target synthesis. Inorganic oxide-based catalysts were taken somewhat more seriously because of a number of key industrial processes which used, and indeed still use, inorganic oxide and zeolite-based heterogeneous catalysts. Two factors, however, have arisen which together have brought supported catalysts to the attention of both academic and industrial chemists. The first is the drive towards more environmentally acceptable chemical processes of all scales. Interestingly, this is not simply an altruistic move on the part of chemists but is increasingly driven by the poor economics of dirty processes and heavy costs of downstream purifications. Funding to my laboratory, for example, confirms a very real stake by the chemical industry in prospects for exploiting polymer-supported catalysts in commodity chemical production. The second factor is the explosive growth in combinatorial and parallel synthesis aimed at speeding up the production of a large diversity of molecules, originally in lead compound discovery groups in the pharmaceutical chemical industry. Using polymer supports and polymer-supported reagents, catalysts, protecting groups, scavengers etc., has allowed the development of a high level of automation and robotics in synthesising libraries of target compounds [81,82]. Indeed the use of supported solid phase synthesis has been extended in the search for novel ligands, catalysts and materials.

A number of world-class synthesis groups are now very active in the area of polymer-supported catalysts [83–86] and as a result of the practical utility which these species offer, both in the laboratory and the plant, commercial exploitation of these is now assured. Precisely which catalyst systems will emerge in technological processes first is difficult to predict, although the versatility of the chiral salen ligands [87] makes these a good bet [86]. Alkene epoxidation remains a key synthetic step and the success in immobilising many of the soluble catalysts relevant to this area suggests that we shall soon see processes running with heterogeneous analogues of these.

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