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Alkene Epoxidations Catalysed by Mo(VI) Supported on Imidazole-Containing Polymers

I. Synthesis, Characterisation, and Activity of Catalysts in the Epoxidation of Cyclohexene

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Polystyrene resins functionalised with hydroxylpropyl aminomethyl pyridine, pyridyl imidazole, and carboxybenzimidazole, polyglycidyl methacrylate resins functionalised with aminomethyl pyridine and pyridyl imidazole, and a polybenzimidazole resin have all been loaded with Mo(VI). The resulting polymer metal complexes have been activated by treatment with *t*-butylhydroperoxide, then used as catalysts in the liquid-phase epoxidation of cyclohexene using *t*-butylhydroperoxide. Polymers containing the imidazole group were particularly active, and unlike the other species did not require preactivation to induce high activity. The complexes formed with the imidazole-containing polymers appear to be monometallic species, whereas the other polymer ligands yield oxybridged bimetallic species. This accounts for the major difference in activity recorded. Possible structures for the catalysts are proposed based on information in the literature. © 1995 Academic Press, Inc.

INTRODUCTION

The development of viable, polymer-supported catalysts for laboratory and industrial oxidation reactions has received recent scientific interest (1–3). An important example of such a process is the industrial manufacture of propylene oxide, which is carried out by the liquid-phase epoxidation of propylene with an alkyl hydroperoxide as oxygen source, catalysed by a homogeneous Mo(VI)(4) or a heterogeneous titanium/silica catalyst (5). Analogous polymer-supported catalysts have utilised anion exchange (6), cation exchange (7, 8), and chelating ion exchange resins (9, 10, 11), the majority being macroporous polystyrene-based resins. Two main factors have limited the technical development of these species. The first is catalyst instability arising from leaching of metal complex from the support. The second is an inherent belief that the normal polymer supports would be too thermo-oxidatively unstable to be used in anything other than mild oxidation processes; certainly an upper operating temperature limit of ~200°C is envisaged. The emergence of polybenzimidazole (PBI) in a porous bead from (12) has therefore been identified as a potentially important and versatile polymer support due to its exceptional thermal stability (>600°C) (see Part III of this work (13)). The present report describes a group of supported Mo(VI) epoxidation catalysts in which imidazole-containing polymers have been used as the supports (Scheme 1).

EXPERIMENTAL

Materials

Polybenzimidazole resin (PBI) was obtained as a gift from the Celanese Corporation (14). The resin was supplied wetted with water. Prior to use it was stirred in 1 *M* NaOH solution for a period of 12 h, washed thoroughly with deionised water until the pH of the washings was neutral, washed with acetone, and dried under vacuum. A polystyrene-based chelating resin functionalised with *N*-(2-hydroxypropyl)aminomethyl-2-pyridine Ps.HPP was obtained from the Dow Chemical Co. (denoted as resin XFS 43084) (15). A glycidyl methacrylate-based (GMA) resin functionalised with 2-aminomethyl pyridine ligands PGMA.AMP was obtained from BP Chemicals Ltd. (16). Both of these resins were subjected to the following treatment prior to use: approximately 20 g of the wet resin was filtered and washed with 2 *M* H_2SO_4, followed by 10% NH_3 solution. The resin was then washed thoroughly with deionised water until pH 7, washed with acetone, and dried under vacuum at 40°C.

An "anhydrous" solution of *t*-butylhydroperoxide (TBHP) in toluene was employed exclusively, since this offers greater thermal and storage stability than anhy-

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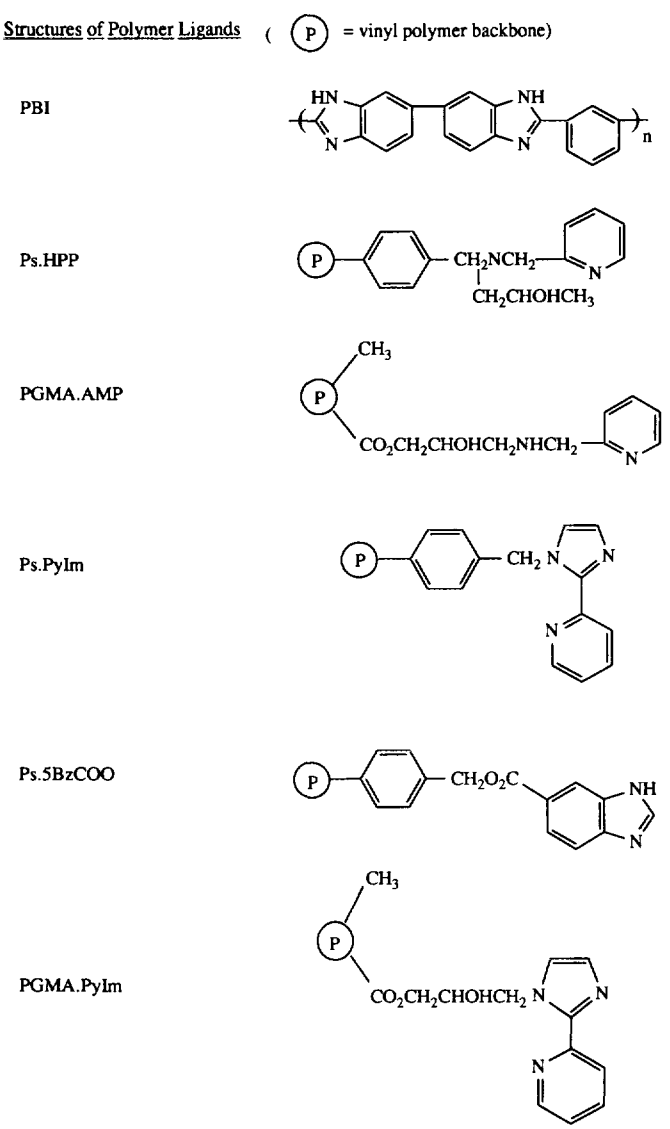


SCHEME 1. Structure of polymer ligands.

drous solutions in halogenated solvents (17) as used in previous work (11). The solution was prepared from aqueous TBHP-70 (Aldrich Chemical Co.) according to the literature method (17). The molarity of each batch was determined using an iodometric titration technique (11).

Chloromethylstyrene (CMS) (60% *m*-, 40% *p*-isomer) (Dow Chemical Co.), divinylbenzene (DVB) (55% *m*-, *p*-divinylbenzene, and 45% *m*-, *p*-ethylstyrenes) (BDH), glycidyl methacrylate (GMA) and ethyleneglycol dimethacrylate (EG-DMA) (Aldrich), cyclohexanol and dodecanol (BDH), 2-ethylhexanol, glyoxal, isopropanol, pyridine carboxyaldehyde, bromobenzene, cyclohexene oxide (Aldrich Chemical Co.), toluene (Analar) (May and Baker), 5-benzimidazole carboxylic acid, and molybdenyl and vanadyl acetylacetonates (Aldrich Chemical Co.) were used as supplied. Cyclohexene (Aldrich Chemical Co.) and 1,2-dichloroethane (Fisons Laboratories) were fractionally distilled prior to use.

SYNTHESIS OF FUNCTIONAL POLYMER SUPPORTS

Polystyrene (Ps)-Based Resins

Polystyrene resins functionalised with 2-pyridyl-2-imidazole (Ps.PyIm) and 5-benzimidazole carboxylic acid (Ps.5Bz.COO) ligands were prepared from a porous chloromethylated polystyrene ($PsCH_2Cl$) resin synthesised via the suspension copolymerisation of CMS (60 vol%) and DVB (40 vol%, i.e., equivalent to 20% crosslinked) using 2-ethylhexanol (in volume ratio 1 : 2 to the co-monomers) as the porogen. The experimental details are available in the literature (15). Elemental microanalysis revealed the chlorine content of their resin to be 14.9%, corresponding to a loading of 4.2 mmol g^{-1} – CH_2Cl groups.

The 2-pyridyl-2-imidazole ligand (PyIm) was synthesised from glyoxal and pyridine carboxaldehyde using a previously published procedure (16). It was attached to the chloromethylated resin as follows: 2-pyridyl-2-imidazole (9.14 g, 0.063 mol) was refluxed with $PsCH_2Cl$ resin (5 g, 0.021 mol-CH_2Cl) in toluene (120 ml) for 12 h. The resin was filtered, washed thoroughly with acetone, extracted with acetone in a Soxhlet apparatus for 24 h, and dried under vacuum at 40°C.

5-Benzimidazole carboxylic acid was attached to $PsCH_2Cl$ via the formation of its sodium salt as follows: 5-benzimidazole carboxylic acid (6.80 g, 0.042 mol) and sodium hydroxide (1.68 g, 0.042 mol) were stirred in ethanol (150 mol) for 4 h. $PsCH_2Cl$ resin (5 g, 0.021 mol-CH_2Cl) was added and the solution refluxed for 24 h. Upon completion, the resin was filtered, extracted with acetone in a Soxhlet apparatus for 48 h, and dried under vacuum at 40°C.

Poly(Glycidyl Methacrylate)(PGMA)-Based Resins

Poly(glycidyl methacrylate) resin functionalised with 2-pyridyl-2-imidazole (PGMA.PyIm) was synthesised from 40% crosslinked macroporous PGMA resin synthesised in-house by the suspension copolymerisation of glycidyl methacrylate (60 vol%) and ethyleneglycol dimethyacrylate (40 vol%) using a porogen (cyclohexanol/dodecanol, 9/1 v/v) present in a volume ratio to monomer 1 : 1. The loading of epoxide groups was calculated to be 4.1 mmol g^{-1} from elemental microanalysis. The synthesis is reported in detail in the literature (16).

The functional PGMA.PyIm resin was synthesised from 2-pyridyl-2-imidazole (5.8 g, 0.040 mol) and PGMA

TABLE 1

Elemental Microanalytical Data, Functional Group Loading, and Salient IR Spectral Data for Resin Supports

Resin	Found (%) C	H	N	Ligand loading (mmol g^{-1})	IR spectral data (cm^{-1})
PBI	65.2	4.4	15.2	5.4	1300, 1450, 1610 (C=N, C=C)
Ps.HPP	75.9	6.8	7.1	2.5	810 (arom. ring); 1450 (C=N)
PGMA.AMP	55.4	6.4	4.5	2.5	1450 (C=N); 3400 (O—H)
Ps.PyIm	71.2	5.9	9.2	2.2	810 (arom. ring); 1450 (C=N) (loss 1260 CH_2Cl)
Ps.5BzCO$_2$	74.8	6.3	1.8	0.4	810 (arom. ring); 1590 (C=O); 3440 (N—H) (loss 1260 CH_2Cl)
PGMA.PyIM	56.0	6.3	4.5	1.1	1450 (C=N); 3400 (O—H)

resin (5 g, 0.020 mol epoxide) using an identical procedure to that described previously for the Ps.PyIm resin.

Elemental microanalytical data functional group loading and salient IR spectral data for the funtionalised resins are given in Table 1.

Preparation of Polymer-Supported Mo Complexes

All supported Mo (and V) complexes were prepared using a ligand exchange procedure in which the resins were reacted with molybdenyl (or vanadyl) acetylacetonate in the stoichiometric ratio 2 : 1 $MoO_2(acac)_2$: functional ligand. A typical procedure for the PBI.Mo metal complex was as follows: PBI resin (5.00 g, 0.027 mol imidazole group) was refluxed with molybdenyl acetylacetonate (17.68 g, 0.054 mol Mo) in toluene for a period of 72 h. Stirring was with an overhead mechanical device in order to prevent attrition of the resin beads. Upon completion, the resin was filtered and extracted exhaustively with acetone in a Soxhlet apparatus for 48 h. During extraction a dark-blue colour was evident in the extracting solution. This disappeared eventually upon repeated introduction of fresh solvent. The supported complex was then dried thoroughly under vacuum.

Mo Loading Analysis of Supported Metal Complexes

The metal loading of the supported complexes was determined as follows. Supported Mo complex (0.1 g, accurately weighed) was ground finely and treated with aqua regia (15 ml) for a period of approximately 48 h. The solution was made up to 100 ml with deionised water and analysed for Mo using atomic absorption spectrophotometry. The metal loading data, corresponding ligand : metal ratios, and IR spectral data for all the supported complexes are given in Table 2.

Catalyst Activation

In previous work (11), it was reported that activation of supported metal complexes with TBHP prior to use was a prerequisite for the occurrence of significant catalytic activity. Accordingly, the supported complexes in this work were activated prior to use in an epoxidation reaction using the following procedure. Supported Mo complex (0.02 g, 0.06 mmol Mo) was refluxed with anhydrous TBHP solution (1.3–1.4 ml, 5 mmol) in 1,2-dichloroethane for a period of 4 h. During this procedure the colour of all the supported complexes changed to yellow. After completion, the beads were filtered off, washed with 1,2-dichloroethane, and used immediately in a reaction. The supernatant liquors from activations and washings were assayed for Mo using AAS in order to determine the amount of Mo leached from the supported

TABLE 2

Mo Loading Data, Ligand : Metal Ratios, and IR Spectral Data for Polymer-Supported Complexes

Polymer catalyst	Loading (mmol g^{-1}) Ligand[a]	Mo	Ligand : metal ratio	IR Bands (cm^{-1}) M=O str.	Mo–O–Mo str	Appearance[b]
PBI.Mo	4.5	1.8	2.5 : 1	950,979	—	Dark blue
Ps.HPP.Mo[c]	2.2	1.3	1.7 : 1	916,933	726	Brown
PGMA.AMP.Mo	1.4	1.1	1.3 : 1	906,940	720	Dark blue
Ps.PyIm.Mo	2.1	0.5	4.5 : 1	960,915	—	Brown
Ps.5BzCO$_2$.Mo	0.41	0.19	2.2 : 1	960,904	—	Green
PGMA.PyIm.Mo[c]	0.99	0.66	1.5 : 1	946,910	—	Green

[a] (1-weight Mo g^{-1} supported complex) × (original ligand loading).

[b] Some variation in colour seen from bead to bead.

[c] *Note* loadings of V on Ps.HPP.V, and PGMA.AMP.V were similar to the Mo data.

TABLE 3

Mo Leached during Activation of Supported Complexes

Complex	Conc. Mo leached (ppm)	(%) Mo leached[a]
Ps.HPP.Mo	1.8	1.4
PGMA.AMP.Mo	2.8	2.7
PBI.Mo[b]	1.4	0.8
PBI.Mo[c]	1.4	0.8
PBI.Mo[d]	1.4	0.8

[a] Expressed as percentage of Mo originally present on resin.
[b] 4 h activation.
[c] 24 h activation.
[d] 48 h activation.

complex during the activation procedure. Table 3 shows the results obtained.

Determination of "Active Oxygen" Content of Activated Supported Mo Complexes

Measurement of the "active oxygen" content of the activated species was carried out in order to provide more information regarding the structure of the complex formed on the polymer during activation and in particular some measure of the content of active sites. An iodometric titration procedure similar to that employed for determining the molarity of the anhydrous TBHP solution was used, but with an accurately weighed amount of activated complex used in place of the TBHP solution. Precedent exists in the literature for the use of titrimetric determination of the concentration of polymer-bound peracid oxidising agents (18). A typical procedure was as follows. Isopropanol (25 ml) and glacial acetic acid (2 ml) were stirred for 2–3 min, sodium iodide/isopropanol solution (10 ml) and the sample of activated polymer complex were added, and the solution refluxed gently for 1 h. Upon completion, the solution was titrated with 0.1 *M* sodium thiosulphate solution using starch indicator to enhance the end-point in the usual manner. Table 4 shows the results obtained for the three polymer catalysts analysed.

TABLE 4

"Active Oxygen" Content of Polymer Catalysts Activated with TBHP

Polymer catalyst	Active oxygen (mmol g^{-1})	Mo loading (mmol g^{-1})	Apparent O : Mo
PBI.Mo	3.2	1.8	1.7 : 1
Ps.HPP.Mo	2.1	1.3	1.6 : 1
PGMA.AMP.Mo	2.8	1.1	2.6 : 1

Catalytic Epoxidations

A typical procedure was as follows. A sample of catalyst (weight equivalent to 0.06 mmol Mo), cyclohexene (8.4 ml, 0.083 mol), bromobenzene (0.5 ml), and 1,2-dichloroethane (0.2 ml) were placed in a twin-necked thermostated reaction vessel equipped with condenser and septum cap, and left to thermally equilibrate at 80°C for a period of 20 min. Anhydrous TBHP solution (1.4 ml, 5 mmol) was added, this point being taken at the commencement of the reaction. Samples were withdrawn by syringe periodically (typically every 20 min) during the 4 h reaction period, and the growth of the cyclohexene oxide concentration was monitored by high-resolution capillary GLC. The cyclohexene oxide concentration for each sample was taken as the mean of three injections.

Instrumentation

Elemental microanalyses were performed on a Carlo Erba Analyser 1106 FTIR spectra of the polymer samples were run as KBr discs on Nicolet 20SXB and Unicam-Mattson 1000 spectrometers. Atomic absorption spectroscopy (AAS) was carried out on a Philips PU1800X instrument. The GLC used was a Carlo-Erba Mega series 5380 high-resolution capillary gas chromatograph with a cold on-column injection facility.

RESULTS AND DISCUSSION

Functionalisation of Polymer Support Resins

The microanalytical and IR data of the functionalised resins presented in Table 1 are indicative that successful functionalisation has taken place. For the polystyrene-based resins, the disappearance of the band at 1260 cm^{-1} associated with the CH_2Cl group, along with the appearance of bands attributable to the pyridine or imidazole-based ligands, show that effective displacement has occurred. The same may be stated of the PGMA.PyIm resin, with the displacement indicated by the appearance of an OH band at 3400 cm^{-1} in the IR spectrum due to the ring opening of the pendent epoxide groups. In the case of the attachment of 5-benzimidazole carboxylic acid, in principle this might occur competitively via both O- and N-alkylation yielding ester links and N-alkylated imidazole groups, respectively. Evidence from the IR spectrum (CO and NH vibrations) suggests that attachment is predominantly via an ester linkage as shown in Scheme 1 (Ps5BzCOO). In all cases the ligand loading achieved is more than adequate for catalyst preparation.

Synthesis and Characterisation of Polymer-Supported Mo Complexes

The ligand exchange of the support resins with molybdenyl acetylacetonate successfully yielded supported Mo complexes with Mo contents in the range 0.2–1.8 mmol g^{-1}, again very adequate for catalytic application. In all cases ligand : metal ratios (Table 2) were >1 suggesting each metal centre to be complexed by at least one ligand. Polymer complexes varied from nondescript green or brown colours to mainly dark blue in the case of PBI.Mo with some beads rather yellow in colour. It is known that dark-blue and yellow colours are indicative of mixed oxide (Mo(V-VI) and Mo(VI) oxidation states, respectively (19). The IR spectra of the complexes showed two bands attributable to terminal Mo=O stretching modes in the region 900–1000 cm^{-1} (20), indicating the presence of supported oxomolybdenum centres. Both the Ps.HPP- and PGMA.AMP-supported Mo complexes also exhibited a band in the 720–730 cm^{-1} region assigned to bridged Mo–O–Mo species. This agrees with previous findings (11) in which an oxo-bridged Mo(V-VI) mixed-oxide structure was proposed for these supported complexes. However, no bands attributable to Mo–O–Mo bridges were found in the resins possessing imidazole-type functionalities, indicative of a different type of structure. PBI.Mo also retained bands in its IR spectrum characteristic of the acetylacetonate ligand (~1265 and 1532 cm^{-1}), whereas Ps.HPP.Mo and PGMA.AMP.Mo showed complete loss of this ligand. Possible structures will be discussed in more detail with reference to the observed catalytic activity in the relevant section later.

Catalyst Activation and "Active Oxygen" Content Determination

It has been established previously by ESR measurements that the activation process in catalysts similar to those described here almost certainly involves oxidation of the supported Mo centres to their highest oxidation state (VI) (9). In the case of the Ps.HPP and PGMA.AMP Mo complexes, Sherrington and Simpson (11) proposed a mechanism in which the Mo–O–Mo bonds were ruptured, along with coordination of TBHP directly to the metal centre, yielding the active species. The "active oxygen" : Mo ratios obtained for the activated supported complexes are all in excess of unity (Table 4) indicating that at least one TBHP moiety is coordinated to each Mo centre. The values above unity are difficult to reconcile and may well arise as a result of unreacted TBHP being present in the pore structure of the resins. A more thorough washing with solvent prior to titration may have reduced these values, but prolonged exposure to solvent also offered the risk of decomposition of the active complex. Overall the values of the active oxygen content of the resins suggest that most, if not all, of the Mo centres are active and accessible under the conditions of the analysis.

The proportion of metal leached from the complexes during the activation process is of the same order as that recorded previously (21). The most important observation is that the amount of metal leached in the case of the PBI.Mo complex is somewhat less than that from the other two complexes, perhaps indicating stronger coordination of the Mo centres by the imidazole functionalities present in PBI. The structure of the ligand and nature of the bonding between the ligand and the metal has been found to have important implications regarding the amount of metal leached from related catalysts during recycling (21) (see also Part II of this work (22)).

Catalytic Epoxidations of Cyclohexene

The results of initial experiments are shown in Table 5. Clearly the soluble species $MoO_2(acac)_2$ is a potent catalyst and this is already well known. Likewise $VO(acac)_2$ is less effective as a result of nonproductive side reactions with TBHP and *t*-butanol. The results for Ps.HPP.Mo after 60 min agree well with our earlier data (11, 21) and show that the nonactivated catalyst has very low activity. The same is true for PGMA.AMP.Mo. Interestingly, the V analogues of these (again nonactivated) show more encouraging activity. However, the most important result is the extremely high activity of PBI.Mo (again nonactivated). This difference is shown more clearly in Fig. 1, where the full conversion curves are reproduced. In all cases polymer Mo catalysts turned yellow during reactions.

The results of activating the catalysts by pretreatment with TBHP are shown in Table 6. As observed previously

TABLE 5

Catalytic Epoxidation of Cyclohexene with TBHP Using Homogeneous and Supported Mo and V Catalysts[a]

Catalyst[b]	Cyclohexene oxide yield (%)		
	20 min	60 min	120 min
$MoO_2(acac)_2$	90.2	92.2	95.9
PBI.Mo	91.0	98.5	100.0
Ps.HPP.Mo	1.1	6.8	23.2
PGMA.AMP.Mo	9.6	12.8	59.6
$VO(acac)_2$	59.4	63.6	73.4
Ps.HPP.V	29.8	40.4	70.4
PGMA.AMP.V	14.0	28.4	35.4

[a] Yield based on conversion of TBHP, i.e., 5 mmol TBHP= 5 mmol cyclohexene oxide = 100% yield. Reaction conditions: [TBHP] = 5 mmol, [cyclohexene] = 83 mmol, [catalyst] = 0.06 mmol, temperature = 80°C.

[b] Polymer catalysts *un*activated.

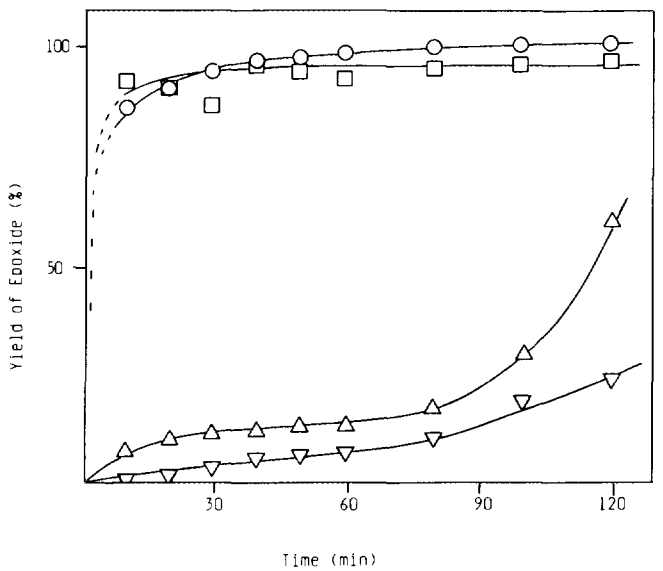


FIG. 1. Conversion curves for epoxidation of cyclohexene by TBHP catalysed by □, $MoO_2(acac)_2$; ○, PBI.Mo; ▽, Ps.HPP.Mo; and △, PGMA.AMP.Mo. Polymer catalysts were nonactivated and conditions were as in Table 5.

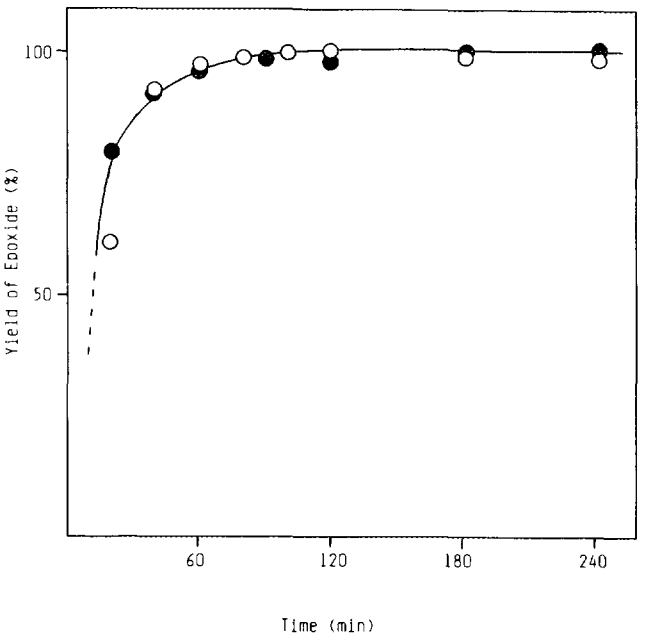


FIG. 2. Conversion curves for epoxidation of cyclohexene by TBHP catalysed by PBI.Mo: ○, nonactivated; ●, activated for 4 h with TBHP at 80°C. Reaction conditions were as in Table 5.

(11, 21) this yields highly active catalysts from all the polymer-supported species. Activation of PBI.Mo, however, does not further increase the activity of this already highly active species. This is shown clearly in Fig. 2, where the conversion curves for the nonactivated and activated species are essentially superimposed.

A very important difference from earlier work is shown in Table 6 for the species Ps.HPP.Mo. For reactions left for 240 min the nonactivated species does indeed become active, and eventually offers reasonable conversion of the alkene to its epoxide. This is also true for PGMA.AMP.Mo and is shown most clearly in the conversion curves in Fig. 3. We have previously believed that supported Mo complexes of this type do not experi-

TABLE 6

The Effect of the Activation Process on Catalytic Activity of Supported Catalysts[a]

Catalyst	Activation conditions	Cyclohexene oxide yield (%)		
		20 min	60 min	120 min
Ps.HPP.Mo	Unact.	1.4	7.9	83.0
	4 h act.	9.6	12.8	99.8
PGMA.AMP.Mo	Unact.	2.2	4.3	94.8
	4 h act.	35.2	82.4	98.4
PBI.Mo	Unact.	60.6	97.1	98.3
	4 h act.	79.6	96.0	99.2
Ps.PyIm.Mo	Unact.	19.6	26.4	87.8
	4 h act.	6.7	9.3	74.1
Ps.5BzCOO.Mo	Unact.	3.4	23.8	~100.0
	4 h act.	11.6	41.5	~100.0
PGMA.PyIm.Mo	Unact.	53.9	84.9	~100.0
	4 h act.	42.3	87.6	~100.0

[a] Reaction conditions identical to those in Table 5.

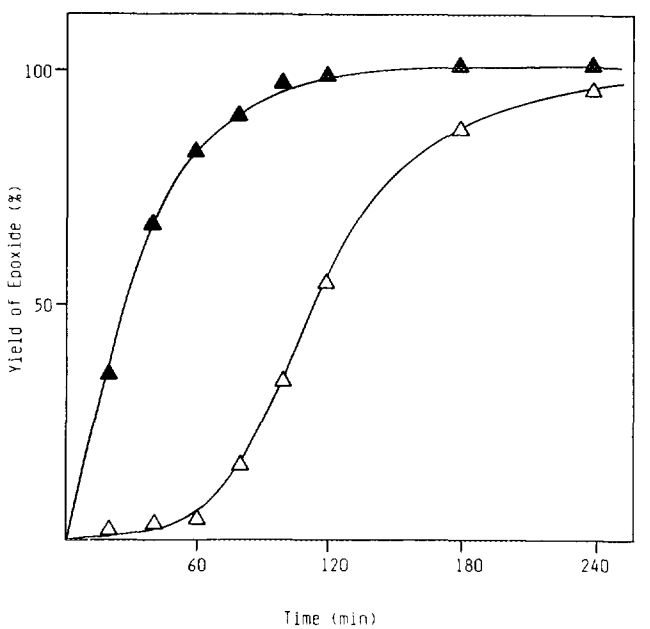
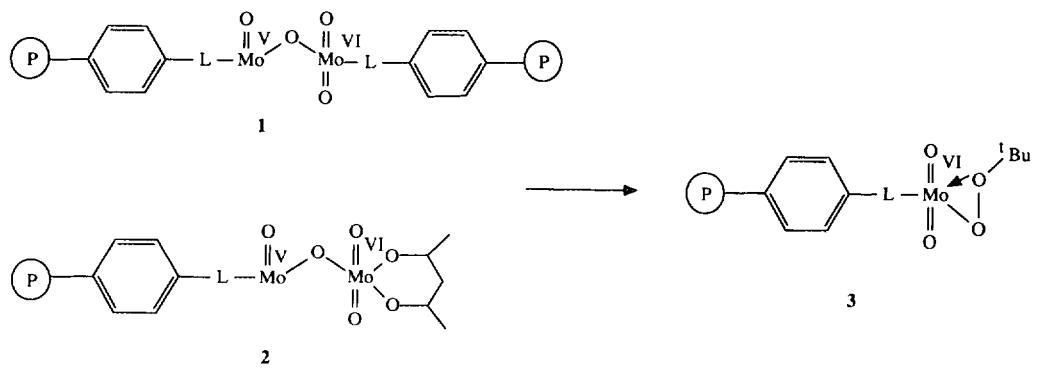


FIG. 3. Conversion curves for epoxidation of cyclohexene by TBHP catalysed by PGMA.AMP.Mo: △, nonactivated; ▲, activated for 4 h with TBHP at 80°C. Reaction conditions were as in Table 5.



SCHEME 2. Proposed structure of Mo complexes formed on PS.HPP and PG.MA.AMP resins.

ence *in situ* activation and have struggled to find a plausible explanation (11). It is now clear that our earlier reactions were terminated too quickly (~60 min) and when left to run longer, active catalytic centres are indeed generated in these polymer catalysts.

Catalyst Structures

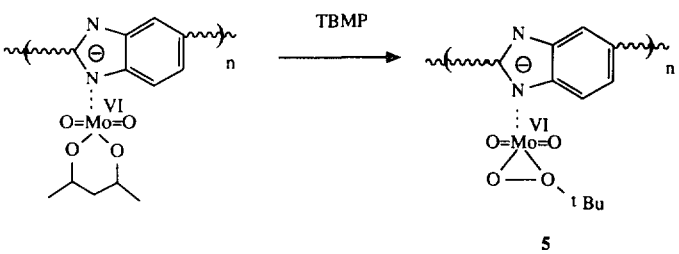
We have argued previously (11) that the Mo complex formed by ligand exchange with $MoO_2(acac)_2$ on polymer supports such as Ps.HPP and PGMA.AMP, both of which carry the hydroxypropylaminomethyl pyridine (HPP) ligand, has an oxo-bridged bimetallic structure (**1**) with both a Mo(V) and a Mo(VI) centre in which both ions are coordinated by a polymer ligand, possibly the alkoxide form of HPP (Scheme 2). Indeed, some polymetallic species, well known in Mo chemistry (23), may be involved. The evidence from the present work supports this idea. We further argued that reaction with TBHP during the activation step cleaves the Mo–O–Mo bridge and yields a mononuclear Mo(VI) centre (**3**) (Scheme 2) analogous to the structures proposed by Sharpless *et al.* (24) and Mimoun (25) and that during this process some Mo is leached. For reasons which remained unclear, *in situ* activation during epoxidation reactions did not appear to occur. Now it is clear that such mononuclear species are generated by reaction with TBHP, and indeed that such a reaction does occur slowly *in situ* in reactions with polymer catalysts previously nonactivated. This oxidation step appears to be rate-controlling and accounts for what is in effect a long induction period with nonactivated complexes (e.g., Fig. 3).

The situation with PBI.Mo is quite different. The nonactivated catalyst is as active as the activated one, and in addition an acetylacetonate (acac) ligand appears to be retained initially by the supported complex. It seems therefore that the polymer complex has the monometallic Mo(VI) structure (**4**) shown in Scheme 3, and that rapid exchange of the residual acac ligand with TBHP generates the active catalytic centre (**5**) with lower opportunity for Mo leaching. This occurs readily *in situ* in expoxidation reactions and no activation step is necessary.

Attempts to isolate a homogeneous analogue of the active Mo(VI) complex on PBI using imidazole and benzimidazole yielded species with many of the right analytical characteristics but which could not be identified unambiguously. Work remains in progress in this direction.

Confirmation that the imidazole ligand does yield complexes quite different from those of earlier ligands (21) was obtained with the polymer catalysts Ps.PyIm.Mo, Ps.5BzCOO.Mo, and PGMA.PyIm.Mo (Table 6). More detailed conversion curves for Ps.5BzCOO.Mo (Fig. 4) and PGMA.PyIm.Mo (Fig. 5) show that reactions involving nonactivated and activated versions of each are very similar.

The role of the imidazole or benzimidazole ligand therefore seems to be crucial and indeed this is also the case in recycling/metal leaching studies (22). The pK_a of the imidazole and acacH molecules is such that at least in the cases of PBI.Mo and Ps5BzCOO.Mo one acac ligand might be displaced from MoO_2acac_2 as acacH by imidazole, the latter coordinating as an anion. Precedent for such an exchange does exist in the literature (26). This exchange would not be possible, however, in the case of



SCHEME 3. Proposed structures of Mo complexes formed on PBI and other imidazole-containing resins.

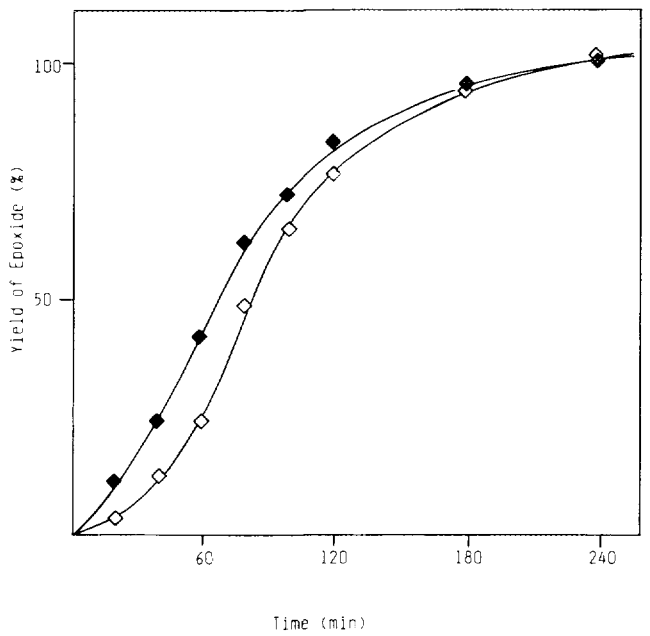


FIG. 4. Conversion curves for epoxidation of cyclohexene by TBHP catalysed by Ps.5BzCOO.Mo: ◇, nonactivated; ◆, activated for 4 h with TBHP at 80°C. Reaction conditions were as in Table 5.

the PsPyIm and PGMAPyIm ligands where the imidazole acidic hydrogen atom has already been lost, and coordination here must be via neutral imidazole residues. Nevertheless, it is interesting to speculate that in the case of

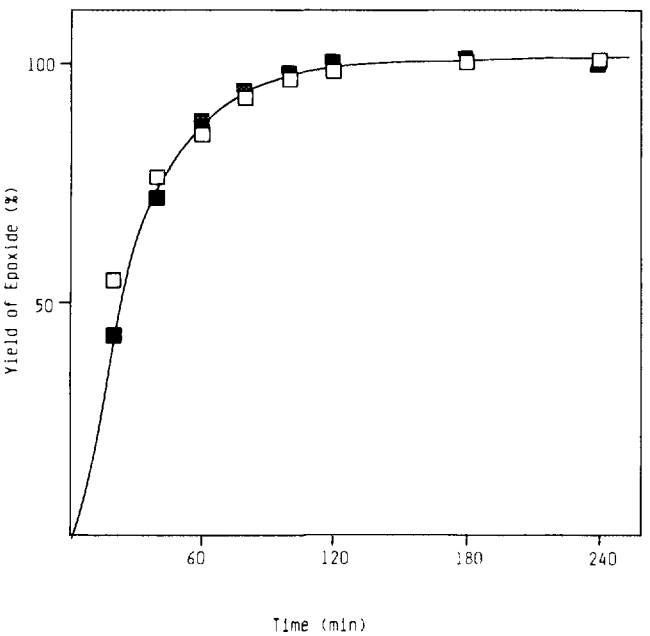


FIG. 5. Conversion curves for epoxidation of cyclohexene by TBHP catalysed by PGMA.PyIm.Mo: □, nonactivated; ■, activated for 4 h with TBHP at 80°C. Reaction conditions were as in Table 5.

PBI.Mo if this anion were to function as a 6π electron donor (analogous to cyclopentadienyl anion) the d^0 configuration of Mo(VI) would formally acquire 6 electrons from the imidazole anion, 8 electrons from the two oxygen ligands, and 4 electrons from the remaining acac ligand, i.e., 18 electrons in all. The existence of π-donation from imidazole towards certain transition metal ions (27) and Mo in particular (28) has been reported, but the bonding is not *of the 6π electron face on type*. However, the pyrrole anion is known to bind to metal centres in this way, and indeed for the lone pair electrons on N to bind simultaneously to a second metal centre (29, 30). Structures analogous to this involving imidazole and benzimidazole, stabilised by immobilisation on a polymer backbone, may therefore not be too unreasonable.

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