JOURNAL OF CATALYSIS 152, 377–383 (1995)

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

II. Recycling of Polybenzimidazole-Supported Mo(VI) in the Epoxidation of Cyclohexene

Matthew M. Miller[1] and David C. Sherrington[2]

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland, United Kingdom

Received May 16, 1994; revised December 19, 1994

Mo(VI) has been supported on a polybenzimidazole resin and used as an epoxidation catalyst in the reaction of *t*-butylhydroperoxide (TBHP) with cyclohexene. A preliminary kinetic study has suggested that mass transfer of TBHP might be rate-limiting. The experimental activation energy is higher than that of an analogous homogeneous reaction catalysed by MoO_2acac_2. Nevertheless, the supported catalyst is highly active and has been recycled nine times with no detectable loss of Mo from the support, but with a decline in activity. Activation of the polymer catalyst by pretreatment with TBHP for periods up to 48 h does not influence the activity of the catalyst on first use; however, higher activity is retained on recycling. The imidazole ligand on the polymer appears to bind the Mo centres very effectively and Mo leaching is not responsible for the decay in activity on recycling. The most likely explanation for this is the blockage of access to catalytic sites in the polymer by accumulation of side-products (oligomer) from cyclohexene or its epoxide.

INTRODUCTION

The prolonged activity of a polymer-supported heterogenised catalyst for applications requiring recycling or fixed-bed operation is perhaps the singular most important factor in its performance. Gradual deactivation of the catalyst by either degradation of the polymer support itself or by leaching of metal from the catalyst is unfavourable from both an economic and, increasingly, from an environmental viewpoint. Polymer-supported analogues of homogeneous Mo(VI) catalysts employed in the industrial liquid-phase epoxidation of propylene with an alkyl hydroperoxide as oxygen source (1) (the Halcon process) have used anion exchange (2), cation exchange (3, 4), and chelating ion exchange resins (5–7) as supports. Most of these reports describe the initial activity of the catalysts but give little or no information regarding the catalytic activity and metal leaching with prolonged use or recycling. A recent study employing polystyrene and polyvinylpyridine-based supports examined in detail the effect of ligand environment upon the recycling activity of the catalysts (8). Resins functionalised with bidentate chelating ligands such as *N*-(2-hydroxypropyl)aminomethyl-2-pyridine were found to produce much more stable catalysts with metal leaching observed to tend towards zero by the end of ten catalytic recycles. Our own work involving highly thermally stable porous polybenzimidazole (PBI) beads (Scheme 1) as a support for Mo(VI) catalysts has shown extremely favourable results for recycling applications in the epoxidation of propene (9, 10). Here we report our studies on the recycling of this catalyst in the epoxidation of cyclohexene, as well as a preliminary study of the kinetic behaviour of the catalyst. We have also prepared a polybenzimidazole-based catalyst which has been derived with an *N*-(2-hydroxypropyl)aminomethyl-2-pyridine in order to provide a comparison of the two different ligands on a common support.

EXPERIMENTAL

Materials

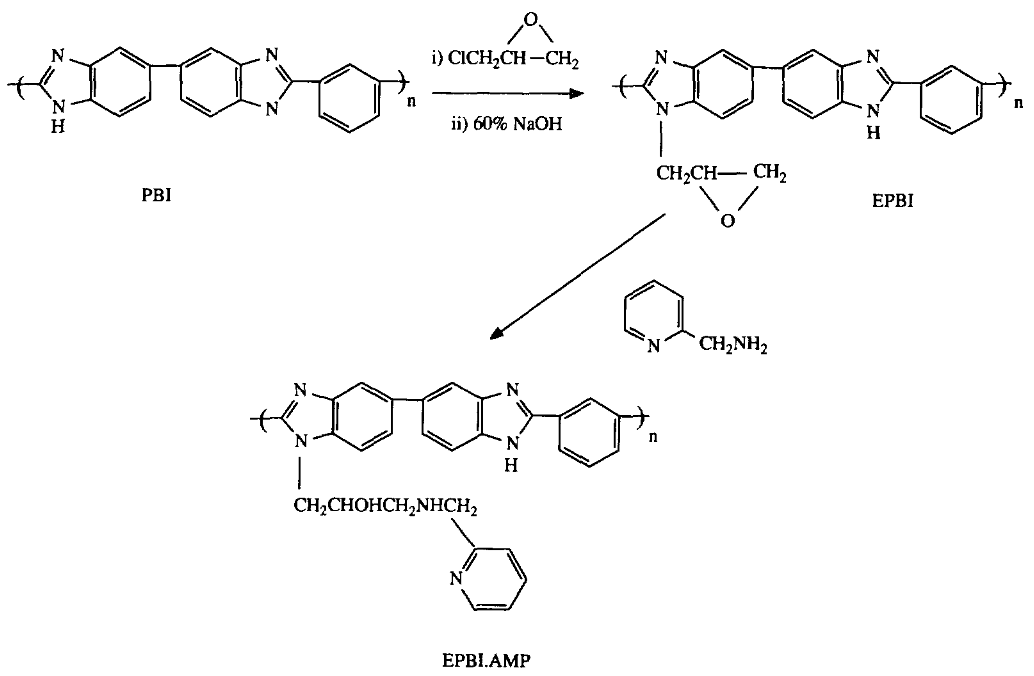
Polybenzimidazole (PBI) resin was a gift from the Celanese Corp.; details are provided in the preceding paper (Part I) of this work (11)). An "anhydrous" solution of *t*-butylhydroperoxide (TBHP) in toluene was employed exclusively throughout and was prepared according to the literature (7, 8, 12) from aqueous TBHP-70 (Aldrich Chemical Co.). The molarity was determined by iodimetry. Aminomethyl-2-pyridine (AMP), bromobenzene, cyclohexene oxide, epichlorohydrin, and molybdenyl acetylacetonate were all used as supplied by the Aldrich Chemical Co. Cyclohexene (Aldrich Chemical Co.) and

---

[1] Present address: Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, U.K.

[2] To whom correspondence should be addressed.

0021-9517/95 $6.00



SCHEME 1. Chemical modification of PBI to introduce aminomethyl-2-pyridine ligands.

1,2-dichloroethane (Fisons Laboratories) were purified by fractional distillation prior to use.

Synthesis of Epoxidised PBI Resin with Aminomethyl-2-Pyridine Functionalities (EPBI.AMP)

This procedure involves introducing epoxy groups onto the secondary NH groups of the PBI backbone, and thus facilitating the attachment of amine chelating ligands via nucleophilic ring-opening of the attached epoxy groups as shown in Scheme 1. The method has been employed previously by Chanda and Rempel (13) to produce metal-selective sorbent resins based on polybenzimidazole. Aminomethyl-2-pyridine was employed as the functional ligand due to its successful use in previous work (8) as a polystyrene and polymethacrylate immobilised chelating ligand for similar Mo(VI) catalysts, and to offer the possibility of comparing the behaviour of this ligand on the PBI support. The procedure was carried out as follows. PBI resin (1 g) was treated with excess 1 *M* NaOH solution at 75°C for 4 h, washed thoroughly with methanol until neutral, and dried using a water pump. Epichlorohydrin (12 ml) was added to the resin and the mixture stirred for 72 h at 70°C. The resulting yellow hydrochloride derivative (HCPBI) was filtered off, washed thoroughly with methanol and deionised H_2O, and treated with 60% NaOH solution for 1 h at room temperature in order to eliminate HCl and yield the epoxy deriva-

TABLE 1

Elemental Microanalytical and IR Spectral Data for PBI and its Derivatives

Polymer resin	Found (%) C	Found (%) H	Found (%) N	Ligand loading (mmol g^{-1})	IR spectral data (cm^{-1})
PBI	65.2	4.4	15.2	5.4[a]	1300, 1450, 1610 (C=N, C=C)
EPBI	56.5	4.7	8.5[b]	—	1035, 784 (epoxide ring)
EPBI.AMP	57.7	5.2	9.5	0.38[c]	1500 (C=N); 3400 (O-H)

[a] Calculated as imidazole ligands.

[b] Low value for N agrees with literature (13) (see Discussion).

[c] Calculated as aminomethylpyridine ligand from N difference.

TABLE 2

Analytical Data for PBI.Mo and EPBI.AMP.Mo Catalysts

	Loading (mmol g^{-1})				
Polymer catalyst	Mo	Ligand	Ligand : metal ratio	IR spectral data (cm^{-1})	Appearance
PBI.Mo	1.9	4.5	2.5 : 1	950, 979 (Mo=O)	Dark blue
EPBI.AM.P.Mo	0.77	0.35	0.45 : 1[a]	952, 975 (M=O)	Brown

[a] Calculated assuming aminomethylpyridine is the ligand.

tive (EPBI). EPBI was filtered off, washed thoroughly with methanol and deionised H_2O, and dried under vacuum.

EPBI resin (0.5 g) was treated with an excess of a 1 : 1 molar ratio mixture of pyridine : aminomethyl-2-pyridine for 48 h at 120°C. The product was filtered, washed with methanol, deionised H_2O, dilute HCl, dilute NaOH, and finally with deionised H_2O until free from alkali, before being dried under vacuum.

The microanalytical data for PBI and its derivatives are given in Table 1, as are relevant IR data for the EPBI and EPBI.AMP resins.

Preparation and Analysis of Polymer-Supported MO(VI) Complexes

PBI.Mo was prepared by ligand exchange using $MoO_2(acac)_2$ as described in Part I of this work. The procedure for determining the Mo content of polymer catalysts was also as before (11). All relevant data are summarised in Table 2.

Catalyst Activation

When required PBI.Mo was activated before use in epoxidation reactions 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 given period. 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.

Catalytic Epoxidations

The typical procedure was exactly the same as that described in Part I (11). The reaction temperature was 80°C.

Kinetic and Solvent Effect Studies

Kinetic studies were made primarily to determine the kinetic orders of each reactive component, whilst hopefully shedding some light upon the mechanism of epoxidation for the supported catalysts. These were carried out using nonactivated PBI.Mo catalyst in the classical fashion by varying the concentration of one component whilst keeping the others fixed. Overall volume differences encountered whilst varying the cyclohexene and TBHP concentrations were compensated for by varying the amount of 1,2-dichloroethane employed.

Solvent effect studies were carried out by substituting the 1,2-dichloroethane used normally with various solvents of differing polarity.

Catalyst Recycling and Metal Leaching

After completion of an epoxidation, the catalyst was removed by filtration from the reaction solution and washed thoroughly with 1,2-dichloroethane. The reaction solution and washings were combined and excess solvent removed by rotary evaporation to yield a yellow residue. This was then digested in aqua regia (15 ml) for a period of 48 h, made up to a set volume with deionised H_2O, and assayed for Mo using standard AAS techniques. Between reaction cycles each catalyst was stored in a solution consisting of TBHP solution (1.4 ml, 5 mmol) and 1,2-dichloroethane (10 ml). Prior to use, it was removed from the storage solution by filtration. Recycling experiments were carried out over a series of 10 runs for each catalyst, with every second run monitored in detail by GLC.

Instrumentation

The techniques and procedures were the same as those in Part I (11).

RESULTS AND DISCUSSION

Synthesis of EPBI.AMP

The synthesis of the EPBI resin was satisfactory. The N content of the product seemed low but nevertheless agreed excellently with the data in the literature (13). The presence of epoxide groups on the PBI backbone was confirmed by the appearance of charcteristic bands in the

IR spectrum at 1035 and 784 cm^{-1}. The reaction of the EPBI resin with aminomethyl-2-pyridine would also appear to have occurred satisfactorily, with an increase in the nitrogen content of the resin observed, indicative of the attachment of the ligand. A band at 3400 cm^{-1} assigned to an –OH group, indicated that ring-opening of the epoxide group by the amine had occurred, as did an additional C=N stretching mode at 1500 cm^{-1}, indicative of the binding of the aminomethyl-2-pyridine group. From the increase in N content of the resin the loading of aminomethyl-2-pyridine groups was estimated to be 0.38 mmol g^{-1}.

Synthesis of Supported Mo Complexes

This proceeded as before (11) with an Mo loading for the PBI.Mo species of 1.9 mmol g^{-1}, and for the EPBI.AMP.Mo complex of 0.77 mmol g^{-1} (Table 2). The ligand : metal ratio for the former was ~2.5 : 1, whereas superficially the value for the latter was ~0.45 : 1. This assumes that only the pendent aminomethyl-2-pyridine ligands are involved in the complexation of Mo, and this is almost cetainly not the case. Nonfunctionalised imidazole residues on the polymer backbone could also coordinate to Mo centres, and indeed they probably do. The IR spectrum of the EPBI.AMP.Mo species indicated the presence of Mo=O groups (14), but no bands characteristic of bridging Mo–O–Mo groups were seen. This contrasts with the complex formed with AMP ligands bound to polygycidylmethacrylate resins (11), and suggests only a small proportion of binuclear species are formed with EPBI.AMP.Mo and that the predominant form is mononuclear. No further evidence, however, is available in this context.

Kinetic and Solvent Effects

The conditions employed in these preliminary studies are 80°C were not ideal for a detailed kinetic analysis since very often initial rates were high and difficult to quantify accurately. The following experimental rate law was, however, deduced:

$$\text{rate} = k_{\text{expl}}\,[\text{TBHP}]^{1.2}\,[\text{cyclohexene}]^{0.1}\,[\text{catalyst}]^{0.1}.$$

The most important conclusion from this is that within the concentration ranges explored the rate is roughly proportional to [TBHP] and essentially independent of the levels of cyclohexene and PBI.Mo used. The first order dependence on [TBHP] is in agreement with other data in the literature (3, 8, 15). More detailed studies are required to confirm these findings and in particular studies at lower temperature would be useful and indeed are now in progress. A tentative explanation for the present results, however, is that mass transport of TBHP within the resin particles plays a significant role in controlling the overall rate.

Varying the temperature of the reactions allowed a preliminary estimate of the overall activation energy for the homogeneously catalysed reaction of ~15 kJ mol^{-1}, and ~25 kJ mol^{-1} for the PBI.Mo catalysed system, and the former is consistent with other data in the literature (16, 17).

The results obtained when using different solvents for the PBI.Mo (nonactivated) catalysed epoxidations are shown in Table 3. Previous work with homogeneous catalysts has reported lower rates in solvents of lower polarity and with nondonor character (e.g., toluene), and has rationalised the observations based on the nature of the transition state in the rate-determining process (15). In this case, however, there is essentially no difference when using toluene in place of 1,2-dichloroethane, presumably reflecting the influence of the polymer support on the reaction rate. Coordinating solvents like alcohols generally compete with substrate at the active metallic centre and this is most obvious here with the small alcohol, methanol. t-Butanol reduces the rate marginally but again its influence seems to be masked by the polymer support.

Catalyst Recycling and Metal Leaching

The results of this part of work are of much more significance. Recycling experiments were carried out using nonactivated PBI.Mo and with samples which had been activated for 4, 24, and 48 h. In addition the recycling of nonactivated EPBI.AMP.Mo was studied. In *all cases* samples were stored under TBHP solution between reaction cycles. The results for the PBI.Mo catalysts are shown in Figs. 1–4 (for conditions see Experimental and Ref. (11)) and the corresponding Mo leaching data appear in Table 4. Data for the EPBI.AMP.Mo catalyst are shown in Table 5.

TABLE 3

Effect of Solvent on Rate of Cyclohexene Oxide Formation in the Epoxidation of Cyclohexene Catalysed by Unactivated PBI.MO[a]

	Cyclohexene oxide yield (%)		
Solvent	20 min	60 min	240 min
1,2 Dichloroethane	98.3	99.2	99.4
Toluene	97.2	99.6	97.2
t-Butanol	89.3	93.1	87.3
Methanol	8.1	19.4	38.8

[a] Reaction conditions as in Experimental, but with [cyclohexene] = 42 mmol instead of 83 mmol (see Part I (11)).

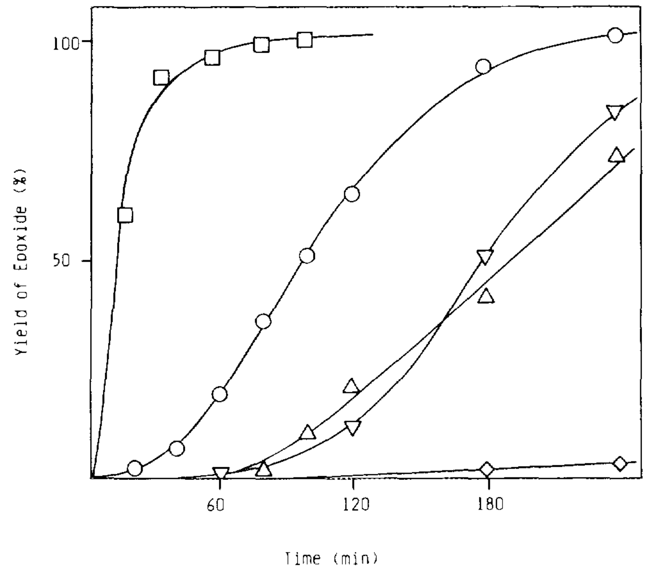


FIG. 1. Conversion curves for recycling of nonactivated PBI.Mo in epoxidation of cyclohexene by TBHP. □, run 1; ○, run 3; △, run 5; ▽, run 7; and ◇, run 9.

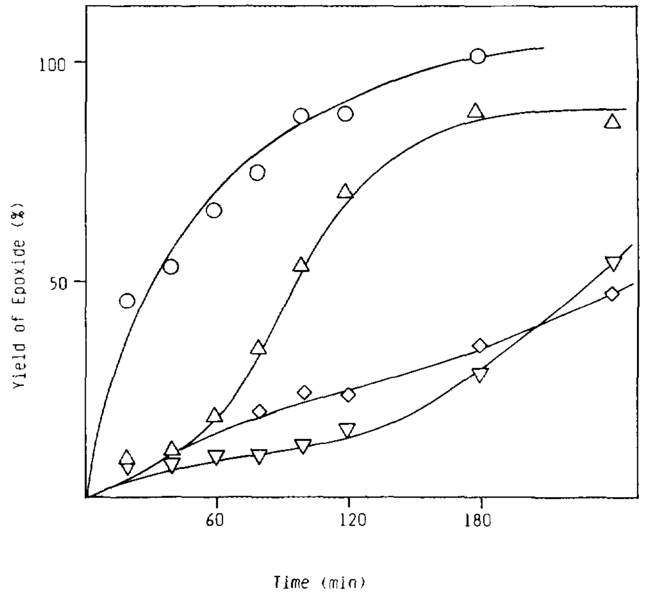


FIG. 3. Conversion curves for recycling of PBI.Mo activated for 24 h before use in epoxidation of cyclohexene by TBHP. □, run 1; ○, run 3; △, run 5; ▽, run 7; and ◇, run 9.

Clearly the activity of the nonactivated EPBI.AMP-supported catalyst is very low and this worsens on recycling. In addition Mo leaching is evident from the outset, and although the levels fall, leaching remains a problem even after 9 runs with the same catalyst sample. The initial low activity is explicable if the Mo centres are complexed mainly by AMP ligand and are bimetallic, since it is now clear that such complexes become catalytically active most effectively by an activation process prior to use in expoxiations (7, 8) (see also Part I (11)). However, there was no evidence in the IR spectrum of EPBI.AMP.Mo for an Mo–O–Mo bridge, and so the structure of the Mo centre in this polymer catalyst remains unclear. What is clear, however, is that the cata-

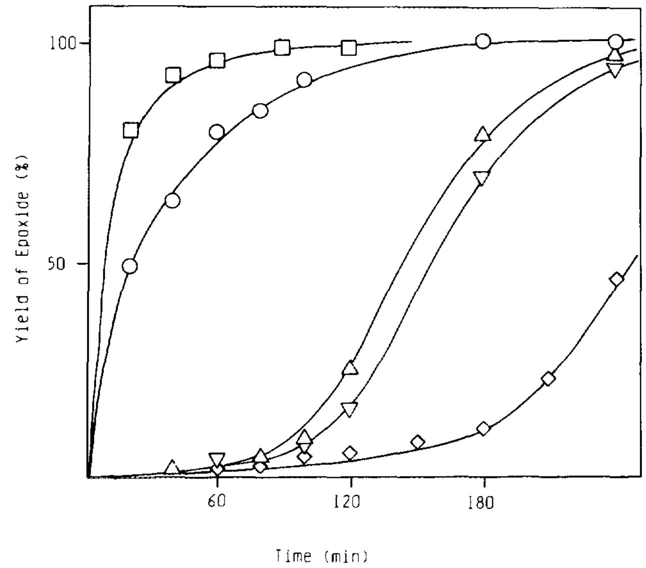


FIG. 2. Conversion curves for recycling of PBI.Mo activated for 4 h before use in epoxidation of cyclohexene by TBHP. □, run 1; ○, run 3; △, run 5; ▽, run 7; and ◇, run 9.

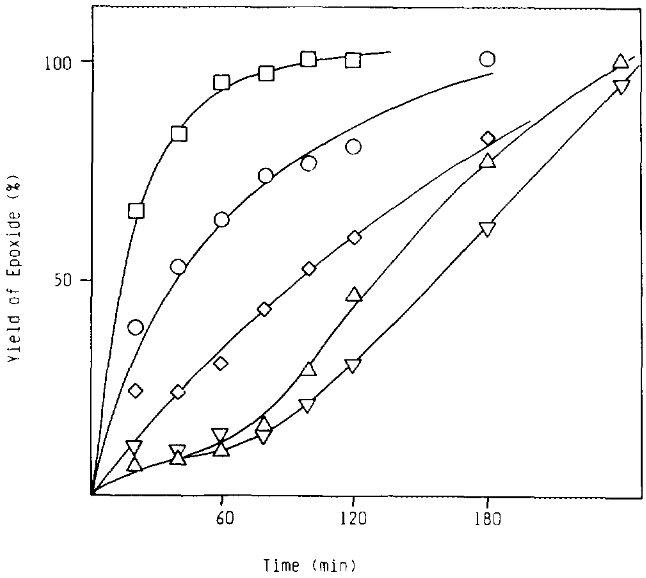


FIG. 4. Conversion curves for recycling of PBI.Mo activated for 48 h before use in epoxidation of cyclohexene by TBHP. □, run 1; ○, run 3; △, run 5; ▽, run 7; and ◇, run 9.

TABLE 4

Mo Leaching Data from Recycling Experiments Using PBI.Mo as Catalyst

	Mo leached from support (%)[a]			
		Activated		
Run No.	Nonactivated	4	24	48
1	~0[b]	2.6	5.2	4.3
3	~0	2.6	~0	~0
5	~0	~0	~0	~0
7	~0	~0	~0	~0
9	~0	~0	~0	~0

[a] Expressed relative to original Mo on the polymer.

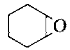
[b] The detection limit of the AAS instrument was ~0.5 ppm which corresponds to Mo% = 0.2. Zero reading therefore implies <0.2% Mo.

lytic activity is low, and the binding of Mo is rather poor, allowing continual leaching.

The results with PBI.Mo are more interesting and complex. Clearly both nonactivated and activated versions of the catalyst are initially very active; indeed, activation for a longer period (24 and 48 h) seems, if anything, to reduce the initial activity a little. This effect has been seen before the polymer-supported aminomethylpyridine complexes of Mo (7). The nonactivated catalyst releases no Mo in the first, *nor indeed in any subsequent runs* (Table 4). (Note that the detection limit of the AAS instrument used is ~0.5 ppm, which translates into ~0.2% Mo: a zero reading therefore corresponds to <0.2% Mo.) There remains therefore an unlikely possibility that undetectably low levels of homogeneous Mo complexes are responsible for the observed catalysis. If so the species would need to be ~two orders of magnitude more active than $MoO_2(acac)_2$. Catalysts activated for 4, 24, and 48 h release up to ~5% Mo in their first use, but thereafter no further release is detected. PBI.Mo is therefore highly stable with regard to metal loss and it is believed that the imidazole ligand plays an important role here, possibly as a 6π electron ligand (see Part I (11)).

TABLE 5

Catalyst Recycling Experiments Using EPBI.AMP.Mo[a,b]

	 O Yield (%)			Mo[c] leached (%)
Run	20 min	60 min	240 min	
1	1.9	4.1	22.1	2.6
3	~0	2.9	12.1	3.0
5	1.6	3.4	6.4	2.2
7	2.7	2.4	5.9	0.9
9	~0	~0	4.7	0.9

[a] For reaction conditions see Experimental section.

[b] Nonactivated.

[c] Expressed as a percentage of Mo originally present on resin.

Despite its high initial activity nonactivated PBI.Mo shows progressive loss of activity on recycling (Fig. 1) until the conversion in run 9 is very low even after 240 min. This is difficult to account for bearing in mind that the Mo leaching is essentially zero. PBI.Mo samples activated for 4, 24, and 48 h show progressively improved retention of activity over 9 runs with increasing prolongation of the activation process (Figs. 2–4). Indeed the species activated for 48 h shows conversions of ~100% after 240 min on all 9 runs. Since the preliminary kinetic study has shown that under the conditions employed (80°C) some diffusion control is operative even with active catalysts, any conclusions drawn from correlations of activity with leaching and recycling have to be tentative. Nevertheless, closer inspection of Figs. 1–4 suggests that activity is not lost on recycling but rather that changes occur in the polymer catalyst which give rise to an induction period. Prolonged activation seems to delay the establishment of this induction period. It might be argued that during activation of the catalyst more catalytic centres are generated on prolonged treatment. However, if this were the case activated catalysts might be expected to show higher activity in Run 1 than in the nonactivated case, as seen for ligands other than imidazole species (8, 11). However, this is not the case. Another possible explanation is that activation causes physical changes in the PBI resin as well as possible chemical changes. Many inorganic oxide-supported catalysts become deactivated by accumulation of product or side-product (e.g., polymer or oligomer) within the pore structure of the support, and this effect can be highly dependent on the porous morphology of the support. When this does arise it is often dependent on the nature of the reactant, e.g., dienes in alkene feedstocks. Interestingly when PBI.Mo is used as a catalyst to epoxidize propylene with TBHP (9) (for details see Part III of this work (10)). These problems on recycling are not observed. The specific changes in catalytic activity and recycling efficiency observed here (Figs. 1–4) appear to be a function of the particular epoxidation being undertaken and it might be that accumulation of small levels of oligomer from cyclohexene or its epoxide are responsible. Different levels of activation might therefore cause changes in the porous morphology of the PBI support, which in turn could influence the rate at which adsorbed contaminants deactivate or physically block the catalytic centres.

ACKNOWLEDGMENTS

We thank the Celanese Corporation for the gift of PBI resin. M. M. M. thanks B. P. Chemicals and the Science and Engineering

Research Council (SERC) for a CASE studentship. D. C. S. acknowledges his Visiting Professorship at Tokyo Institute of Technology funded by Monbusho which allowed this manuscript to be finalised and also acknowledges the travel funds provided by The British Council.

REFERENCES

1. Kollar, J., U.S. Patent 3 3 50 422, 1967; 3 357 635, 1967; 3 507 809, 1970; 3 625 981, 1971 to Halcon International.
2. Sobezak, J., and Ziółkowski, J., *J. Mol. Catal.* **3,** 165 (1978).
3. Ivanov, S., Boeva, R., and Tanielyan, S., *J. Catal.* **56,** 150 (1979).
4. Boeva, R., Kotov, S., and Jordanov, N. I., *React. Kinet. Catal. Lett.* **24,** 239 (1984).
5. Bhaduri, S., and Khwaja, H., *J. Chem. Soc. Dalton,* 415 (1983).
6. Yokoyama, T., Nishizawa, M., Kimura, T., and Suzuki, T. M., *Bull. Chem. Soc. Jpn.* **58,** 3271 (1985).
7. Sherrington, D. C., and Simpson, S., *J. Catal.* **131,** 115 (1991).
8. Sherrington, D. C., and Simpson, S., *React. Polym.* **19,** 13 (1993).
9. Miller, M. M., and Sherrington, D. C., *Chem. Soc. Chem. Commun.* 55 (1994).
10. Miller, M. M., and Sherrington, D. C., *J. Chem. Soc., Perkin II* 2091 (1994).
11. Miller, M. M., and Sherrington, D. C., *J. Catal.* **152,** 368 (1995); Miller, M. M., Ph.D. Thesis, University of Strathclyde, 1993.
12. Sharpless, K. B., and Verhoeven, T. R., *Aldrichimica Acta* **12,** 63 (1979).
13. Chanda, M., and Rempel, G. L., *J. Polym. Sci. A: Polym. Chem.* **27,** 3237 (1989); *React. Polym.* **16,** 29, (1991); *React. Polym.* **17,** 159 (1992).
14. Cotton, F. A., and Wing, R. M., *Inorg. Chem.* **4,** 867 (1965); Moore, F. W., and Rice, R. E., *Inorg. Chem.* **7,** 2510 (1968).
15. Gould, E. S., Reed, J. W., and Su, C., *Inorg. Chem.* **12,** 337 (1973).
16. Mimoun, H., Seree du Roch, I., and Sajus, L., *Tetrahedron* **26,** 37 (1970).
17. Arakama, H., Moro-Øka, Y., and Ozaki, A., *Bull. Chem. Soc. Jpn.* **47,** 2958 (1974).