Supported catalytic epoxidation of polyisobutylene with alkene chain ends

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Polystyrene beads functionalised with cobalt acetylacetonate or 1-phenylacetylacetonate were used as catalysts in the aerobic epoxidation of oligoisobutylene with alkene chain ends. The beads were produced in a range of porosities (22–45 vol.%) and were fully characterised by SEM and porosimetry.

Keywords: polystyrene bead, aerobic epoxidation, polyisobutylene, cobalt, acetyl acetonate

The use of molecular oxygen as an oxidant is a useful approach for the atom efficient oxidation of organic compounds and mimics some of the oxidation processes observed in nature. The catalytic aerobic oxidation of alkenes using cobalt complexes in conjunction with a sacrificial aldehyde or acetal reductant is a useful route to epoxides and nitrogen and oxygen donor ligand systems have been used.[1-14] *Iso*butylene oligomers (OIBs) are produced mainly from C4 streams of petroleum cracking processes and several living polymerisation routes to end functional OIBs are known.[15] The commercial product is produced in non-living processes that yield materials with alkene chain ends. OIBs have been proposed as potential components of amphiphilic networks with uses in biomedical applications[16] and during a programme directed at the preparation and application of these biomaterials we developed a catalytic immobilised process, which we describe here, for the preparation of epoxidised OIBs.

Experimental

Polystyrene beads – suspension polymerisation

Polyvinylpyrrolidinone (2.5 g, Aldrich) dissolved in deionised water (400 ml) was added to a fluted reaction vessel equipped with a 4 blade overhead stirrer. To this was added (in the amounts given in Table 1) styrene (S), vinyl benzyl chloride (VBC), divinylbenzene/ethyl vinyl benzene (DVB) mixture (55 mol % divinyl benzene Aldrich) and dodecane or toluene. This mixture was stirred at a speed of 350 rpm and azobis(isobutyronitrile) (0.5 g) was added. The reaction vessel was maintained at 80 °C under a nitrogen atmosphere for 5 h. Then the mixture was allowed to cool with stirring. The beads produced by this process were filtered off, washed with water and then washed with acetone for 16 h.

Acetyl acetonate functionalised beads

Beads (5.00 g) prepared as above and anhydrous DMF (50 ml) were added to a round bottom flask fitted with a condenser. Sodium iodide (1.5 g, 10 mmol) and sodium acetyl acetonate monohydrate (1.22 g, 87 mmol) were then added. The mixture was heated at 70 °C for 18 h whilst being agitated by bubbling N_2 through the solution. The reaction mixture was cooled and the beads were filtered off and washed with acetone. The beads were dried under vacuum.

Benzoylacetonate functionalised beads

Beads (5.00 g) prepared as above and anhydrous DMF (50 ml) were added to a round bottom flask fitted with a condenser. Sodium iodide (1.5 g, 10.0 mmol), 1-benzoylacetone (1.64 g, 10.1 mmol) and DBU (1.54 g, 10.1 mmol) were added. The mixture was heated at 70 °C for 18 h whilst being agitated by bubbling N_2 through the solution. The reaction mixture was cooled and the beads were filtered off and washed with acetone. The beads were dried under vacuum.

Attachment of undecoxy spacer

Sodium hydride (1.0 g, 41.6 mmol) was added to a solution of 11-bromo-1-undecanol (6.17 g, 24.6 mmol) in anhydrous DMF (70 ml) under a nitrogen atmosphere. After 1 h benzyl chloride functional beads (5.00 g) were added and the reaction mixture was heated and maintained at 70 °C for 16 h whilst being agitated by bubbling N_2 through the reaction mixture. The reaction mixture was cooled and the beads were filtered off and washed with acetone. The beads were dried under vacuum. These beads were further functionalised by reaction with either 1-benzoylacetone DBU/NaI or with sodium acetylacetonate/NaI, using the same procedure as that described above for the methylene benzoylacetonate and methylene acetylacetonate functionalised beads.

Cobalt complexation

An ethanolic solution of cobalt chloride hexahydrate (0.33 g in 60 ml) was gently refluxed in the presence of a particular sample of beads (1.00 g) functionalised with the appropriate ligand for 48 h. Once cooled the beads were filtered off and washed with absolute ethanol until the washings were colourless. The cobalt content of these resins was measured by carrying out ICP-AA on acid washings (conc. nitric acid).

Supported catalytic epoxidation

A round bottom flask fitted with a condenser was charged with Ultravis 1000 (BP Chemicals) (8.9 g), a supported cobalt(II) catalyst (0.12 g, 0.19 mmol), 2-methylpropanal (2.5 ml, 0.027 mol) and 1,2-dichloroethane (DCE) or hexane (50 ml). The mixture was heated at 60 °C and O_2 was bubbled through the solution for 16 h. Once cooled, the beads were filtered off and washed with hexane. The reaction mixture and washings were combined and the solvent was removed under vacuum. The product was a resinous viscous liquid. Conversions were obtained from 200 MHz ^1H NMR spectra.

Instrumentation

SEM measurements were carried out after gold spluttering onto fractured surfaces of the beads with a JEOL 5600 instrument. Porosity measurements were provided by mercury intrusion using a Poresizer® 9320 instrument. 200 MHz ^1H NMR spectra were obtained with a Varian Mercury instrument. ICP-AA was carried out with a CIROS CCD, Spectro Analytical, instrument. Particle sizes were determined by sieving.

Results and discussion

Preparation of polystyrene supported catalysts

A range of chloromethyl-functional polystyrene supports were prepared. The beads were prepared by suspension terpolymerisation of styrene (S), divinyl benzene (DVB) and vinyl benzyl chloride (VBC)

Table 1 Formulations and properties of vinyl benzyl functionalised PS beads

Bead	S Feed/g	VBC/g	DVB/g	Toluene/g	Decane/g	Yield/ wgt.%	Mol% Cl Theoretical	Actual
PS 1	10.0	10.0	20.0	10.0	10.0	93.5	5.82	4.72
PS 2	10.0	10.0	20.0	5.0	15.0	91.0	5.81	4.81
PS 3	10.0	10.0	20.0	0.0	20.0	91.0	5.81	4.67
PS 4	15.0	5.0	20.0	10.0	10.0	87.0	2.91	2.42
PS 5	17.5	2.5	20.0	10.0	10.0	96.4	1.46	1.27

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in the presence of either toluene or decane as porogens. The formulations and elemental analysis data are given in Table 1. The elemental analysis data showed that 80–85% of the VBC was incorporated into the polymer. The beads were very regular and spherical. Increasing the amount of decane in the formulation increased the opacity of the beads. The polymerisations produced beads in the 10^2 μm range. Typically 20 wgt% of the beads had diameters in excess of 1 mm and the fraction with diameters less than 1 mm had average diameters of approximately 700 μm.

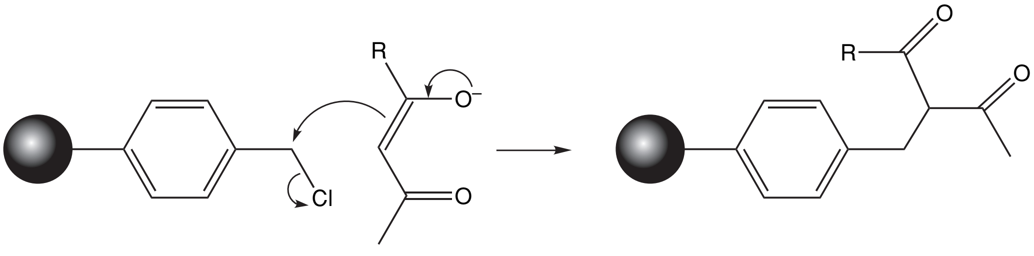
Next the beads were functionalised by base-catalysed enolate reaction, with either acetylacetonate, **1**, or 1-benzoylacetonate, **2**, at the chloromethyl group as shown in Scheme 1. The reactions with **2** proceed to higher final conversion than those carried out with **1** (see Table 2). FTIR spectroscopy indicated the presence of the ligands derived from either **1** (C=O stretch at 1700 cm^{-1}) or **2** (C=O stretches at 1680 and 1700 cm^{-1}). SEMs of each of the beads, following freeze fracturing, are shown in the supporting data. These micrographs clearly illustrated the porous nature of the beads and each bead appears to be formed from agglomerates of phase separated polymer with the primary particles having diameters in the sub-10^2 nm range. Mercury intrusion measurements where used further to characterise the beads. The results are given in Table 2. As can be seen from these data the expected trend was observed. That is as the concentration of decane increased: the porosity, surface area and pore size increased.

The beads of the highest porosity, PS 3, were also functionalised by reaction with sodium 1-bromo-11-oxyundecane followed by base-catalysed reaction with **1** or **2** to give beads in which $n = 11$. However, elemental analysis showed these beads had a more chemically heterogeneous nature than beads produced by direct reaction of the VBC residues with **1** or **2**. This heterogeneity arose from incomplete reaction between sodium 1-bromo-11-oxyundecane and the VBC residues, which left residual methylene chloride moieties that reacted with **1** or **2**. This was observed as a decrease in chlorine content following reaction of the undecanyl bromide functionalised beads with **1** or **2**. However, this decrease in chlorine content is also in part due to reaction of iodide with VBC residues. Therefore, unfortunately it was not possible to estimate the ligand loading using the elemental analysis data.

Epoxidations

The results of the epoxidations of OIB are given below in Tables 3 and 4.

The results of the cobalt analysis clearly indicate that the amount of catalyst bound to the resin, when ligand **2** is used, exceeds by an order of magnitude the amount bound to resins functionalised with ligand **1**. This effect is probably, in part, a consequence of the higher degree of functionalisation achieved with ligand **1** (see functionalisation yields of Table 2). However, these differences in functionalisation yield are insufficient fully to explain the magnitude of the change in the cobalt contents. This is best illustrated by comparison between the materials based on PS1. The two functionalisation yields are 57 and 78 % but the amount of cobalt contained on the resin functionalised by ligand **2** is 14 times that of the resin functionalised by ligand **1**.



1 R = H
2 R = Ph

Scheme 1 Reaction of β–diketone ligand in a polymer analogous reaction

Table 2 Characterisation data for functional beads functionalised wih either **1** or **2**: a functionalisation yield is the yield of VBC residues modified with AcAc or PhAcAc calculated from the elemental analysis data (using the combined Cl and I contents)

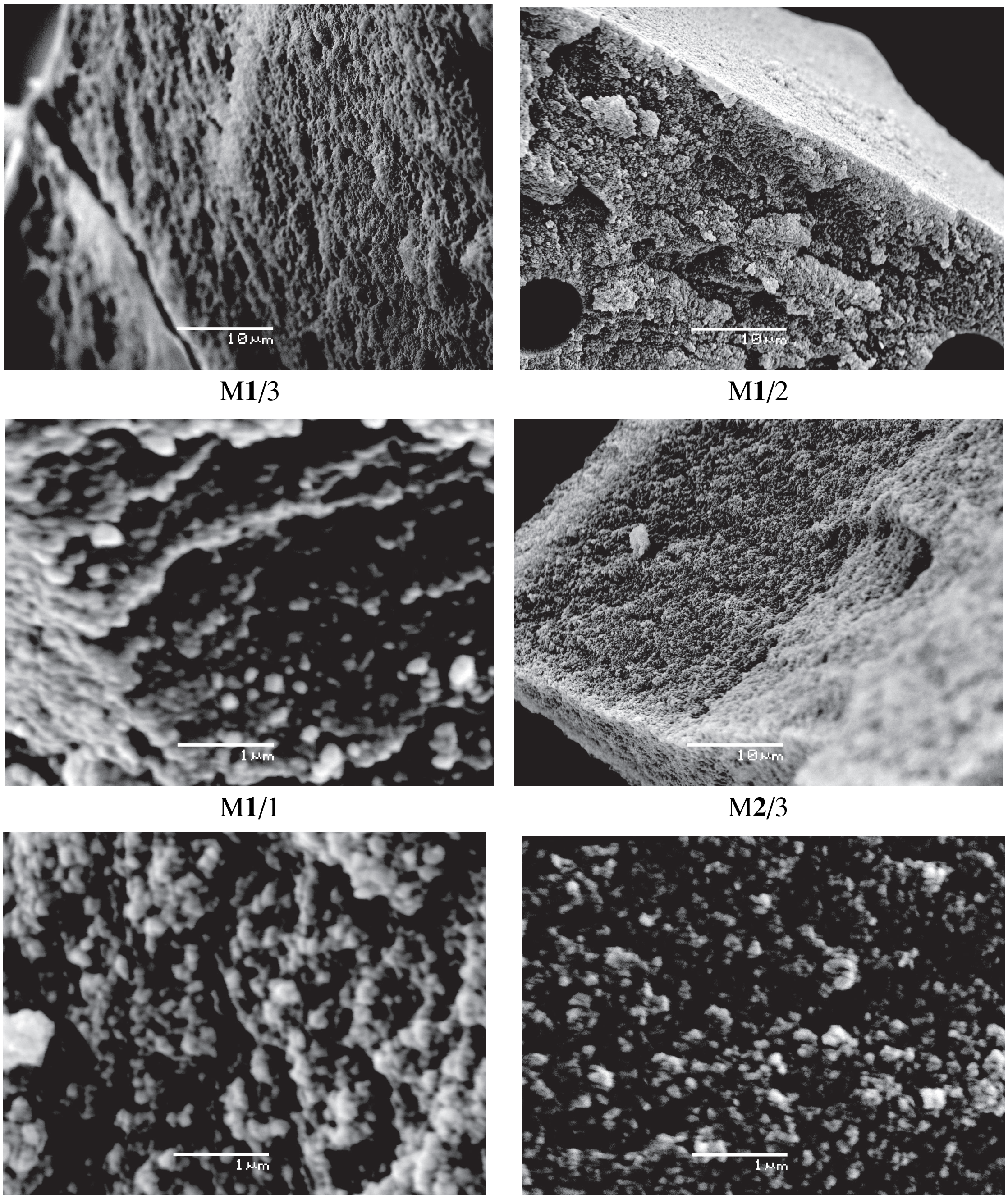
Starting bead	Product ref.	Ligand	Functionalization Yield (%)^a	ligand loading/ mmol g^{-1}	Porosity/%	Mean dia /nm	SA/m^2g^{-1}
PS 3	M**1**/3	**1**	25	0.32	45	41	114
PS 2	M**1**/2	**1**	45	0.68	36	27	103
PS 1	M**1**/3	**1**	57	0.75	26	20	75
PS 3	M**2**/3	**2**	71	0.94	44	35	121
PS 2	M**2**/2	**2**	69	0.93	33	26	84
PS 1	M**2**/1	**2**	78	1.04	22	15	63

Table 3 Conversions of OIB alkene in to epoxide following catalytic aerobic oxidation with various supported co- complexes.

Bead ref.*	Temp.	Solvent	Ligand	Spacer	Porosity	Co content/mmol g^{-1}	%converson of alkene
M**1**/3	60	DCE	**1**	CH_2	45	0.008	0.00
M**1**/2	60	DCE	**1**	CH_2	36	0.007	0.00
M**1**/1	60	DCE	**1**	CH_2	26	0.008	0.00
M*2/3*	60	DCE	**2**	CH2	44	*0.141*	*86*
M**2**/2	60	DCE	**2**	CH_2	33	0.153	53
M**2**/1	60	DCE	**2**	CH_2	22	0.109	59
M**1**/1	60	Hexane	**1**	CH_2	26	0.008	46

Table 4 Epoxidations carried out with undexoxy spacers between polystyrene surface and ligand

Bead ref.	Temp.	Solvent	Ligand	Spacer	Co content/mmol g^{-1}	%Converson of alkene
U**1**/3	60	DCE	**1**	$OC_{11}H_{22}$	0.082	0.00
U**2**/3	60	DCE	**2**	$OC_{11}H_{22}$	0.134	46
U**1**/3	60	Hexane	**1**	$OC_{11}H_{22}$	0.082	40
U**2**/3	60	Hexane	**2**	$OC_{11}H_{22}$	0.134	44
U**1**/3	60	No Solvent	**1**	$OC_{11}H_{22}$	0.082	13



M**1**/3 M**1**/2

M**1**/1 M**2**/3

M**2**/2 M**2**/1

SEMs of the freeze fractured surface of the beads prepared by direct attachment to chloromethyl styrene residues, magnification = x 25000, labels refer to the designations in Table 3

The next observation to be made from these data is that successful supported epoxidation of the chain end epoxide groups of OIB required the use of ligands based on **2** rather than **1**. On the other hand the non-immobilised catalyst, cobalt(II) acetylacetonate, was successfully used to epoxidise OIB (80 mol % conversion of alkene in 8 h at 60 °C). We have previously shown that stabilised 1,3-diketone ligands such as **2** produce more effective epoxidation catalysts than catalysts that use the ligand **1**.[10] However, in this instance there is a large decrease in activity associated with immobilisation of **1** that may be due to the 10-fold lower cobalt contents associated with the use of **1**. There is some indication that successful, *i.e.* high conversion, epoxidation is best achieved with the beads of higher porosity. Thus in the series of beads M**2**/1-M**2**/3 we observed that the beads with 44 vol % porosity yield high conversion of alkene into epoxide whilst more moderate conversion was achieved with the beads with average porosity of 26 vol.%. The final result of this Table shows that these epoxidations can also be controlled by careful choice of solvent. Thus, we have observed that while epoxidation with a low porosity bead using ligand **1** could not be achieved when DCE was used as the solvent the same reaction carried out in hexane produced moderate conversion of the alkene into epoxide.

Next a second series of beads in which there was a longer spacer between the polystyrene surface and the ligand was prepared. All of these beads were prepared using the high porosity procedure (*i.e.* decane as porogen). The results of epoxidation with these beads are shown in Table 4. In agreement with the data given in Table 2 we have observed that epoxidations carried out in DCE require the more active ligand based on structure **2**. However, this difference was not evident when the reaction was carried out in hexane and thus epoxidations of OIB in this medium more resemble the non-immobilised variant, in which differences between the catalysts based on **1** or **2** could not be discerned. The data also point to the importance of the ligand structure and add to the data presented above on the large difference in reactivity, in DCE, on changing the ligand. In the epoxidations given in Table 4 the cobalt contents were 10 times higher than those obtained from beads in which the ligand was directly attached to the bead. However, despite this increase in cobalt loading, the epoxidations in DCE with ligand **1** were still unsuccessful.

Conclusion

We have shown that several variables have an effect on the supported cobalt catalysed aerobic epoxidation of oligoisobutylenes containing a mixture of terminal alkene groups. The highest yields were obtained with materials of highest porosity (45 vol.%) and with acetylacetonate ligands containing groups capable of further stabilising the enolate. Also, the uptake of cobalt was more effective in these latter materials. All of the synthesised beads, where shown to be macroporous, had porosities ranging from 22 to 45 vol%. Finally the solvent medium also plays a role, so that hexane, a good solvent for polyisobutylene, was found to give higher yields of epoxide than DCE.

We thank EPSRC (UK) and BP-Amoco Chemicals for providing fellowships for Dr. P. Cross and Dr. R. Hunter. We would like to thank Ms. B. Lane (Engineering Materials, University of Sheffield) and Ian Staton (Department of Chemistry, Centre for Analytical Sciences) for providing the porosity and cobalt content data respectively.

Received 14 March 2005; accepted 6 June 2005
Paper 05/3128

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