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COMMUNICATION

An efficient recyclable peroxometalate-based polymer-immobilised ionic liquid phase (PIILP) catalyst for hydrogen peroxide-mediated oxidation†

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A linear cation-decorated polymeric support with tuneable surface properties and microstructure has been prepared by ring-opening metathesis polymerisation (ROMP) of a pyrrolidinium-functionalised norbornene-based monomer with cyclooctene. The derived peroxophosphotungstate-based polymer-immobilised ionic liquid phase (PIILP) catalyst is an efficient and recyclable system for the epoxidation of allylic alcohols and alkenes, with only a minor reduction in performance on successive cycles.

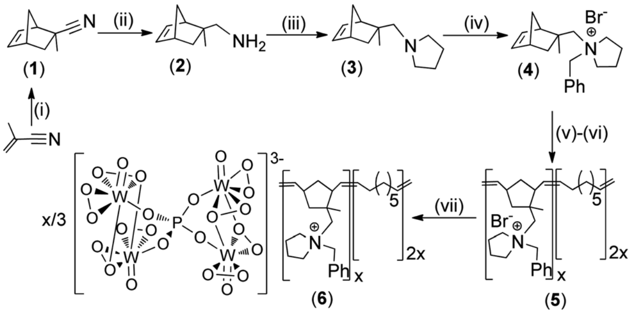
Introduction

Polyoxometalates (POM) are an architecturally and structurally diverse[1] and fascinating class of redox active[2] anionic transition metal–oxygen-based materials. They have been shown to be efficient Brønsted acid catalysts and highly selective oxidation catalysts for a host of commercially important transformations.[3] Surface immobilisation of polyoxometalates and their derived peroxometalates has been intensely investigated as a potentially practical approach to developing a continuous flow process, improving robustness and recyclability as well as overcoming the problem of catalyst leaching normally associated with liquid–liquid biphasic systems. A number of strategies have been developed for the heterogenisation of these catalysts including electrostatic anchoring to ionic liquid-modified silica,[4] nanosized ionic dendritic polyammonium polycations,[5] tripodal organic polyammoniums,[6] alkylated polyethyleneimine,[7] cationic hydrophobic silica xerogels[8] and a poly(ethylene oxide–pyridinium) matrix;[9] in some cases the activity and selectivity matched that obtained under homogenous conditions.

As part of a recently initiated programme to explore and develop the concept of polymer-immobilised ionic liquid phase (PIILP) catalysis we used ring-opening metathesis polymerisation (ROMP) to prepare new cation-decorated polymeric supports, reasoning that the well-behaved living nature of this process and the functional group tolerance of the catalyst would enable surface properties, microstructure, ionic microenvironment, stability and porosity to be modified in a rational and systematic manner, which would enable catalyst–surface interactions, substrate accessibility and efficiency to be optimised, property–function relationships to be elucidated and new activity–selectivity relationships to be established. Herein, we report that peroxometalates can be immobilised on a pyrrolidinium-decorated norbornene-based polymer and this material is an efficient catalyst for the oxidation of allylic alcohols and alkenes. The catalyst can also be recovered and reused with only a minor reduction in performance.

Result and discussion

The pyrrolidinium-based monomer **4** was prepared according to Scheme 1. The BCl_3-catalysed Diels–Alder cycloaddition between methacrylonitrile and cyclopentadiene was conducted in



Scheme 1 *Reagents and conditions*: (i) cyclopentadiene, BCl_3; (ii) $LiAlH_4$, Et_2O; (iii) 1,4-dibromobutane, K_2CO_3, MeCN reflux 15 h; (iv) $PhCH_2Br$, acetone; (v) *cis*-cyclooctene, 2 mol% $[RuCl_2(PCy_3)_2(=CHPh)]$, $CHCl_3$, 40 °C, 15 h; (vi) ethyl vinyl ether, $[P(CH_2OH)_4]Cl$, KOH, excess KBr, $CHCl_3$, 50 °C; (vii) $H_3[PO_4\{WO(O_2)_2\}_4]_{(aq)}$, pyridine, EtOH.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation of compounds **1–4**, polymers **5** and **6**, details of catalysis and for compound **4** details of crystal data, structure solution and refinement, atomic coordinates, bond distances and angles and anisotropic displacement parameters in CIF format. CCDC 853818. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2gc16679h

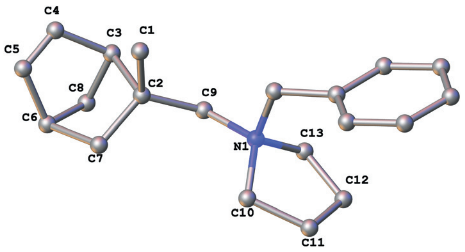


Fig. 1 Molecular structure of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide (**4**), confirming the stereochemistry of cycloaddition. Hydrogen atoms, the water molecule of crystallisation and the bromide anion have been omitted for clarity.

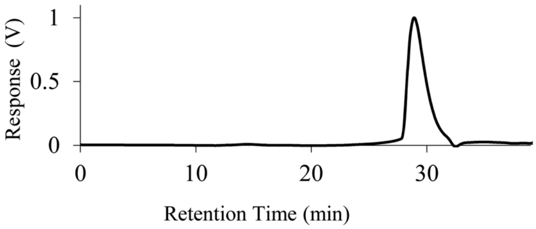


Fig. 2 Differential refractive index (dRI) GPC trace of polymer **4** in DMF (0.6 mL min^{-1}).

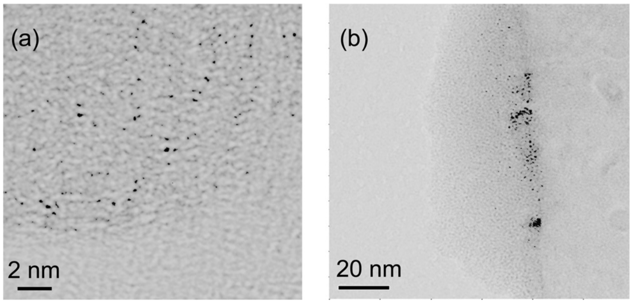


Fig. 3 TEM images of **5** (a) before catalysis and (b) recovered catalyst after use in the hydrogen peroxide-mediated epoxidation of *cis*-cyclooctene showing some aggregation.

the absence of solvent and occurred with high *exo*-diastereoselectivity to give **1** as a 89 : 11 mixture of *exo* and *endo* diastereoisomers. $LiAlH_4$ reduction of **1** gave the corresponding methylamine adduct **2**, a versatile intermediate for the synthesis of a range of onium-based monomers. The pyrrolidine ring of **3** was formed by intramolecular dialkylation of **2** with 1,4-dibromobutane and subsequently quaternised by reaction with benzyl bromide in acetone to afford the desired pyrrolidinium-based monomer **4**, which was isolated as a spectroscopically and analytically pure white solid. Importantly, although monomer **4** requires a linear four step synthesis, it can be accomplished without purification by column chromatography, which greatly simplifies the process and reduces the overall cost.

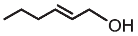
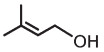
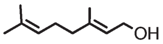
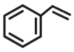
The Lewis acid-catalysed Diels–Alder cycloaddition between methacrylonitrile and cyclopentadiene has recently been reported to occur with high *endo*-diastereoselectivity,[10] therefore a single crystal X-ray structure determination of **4** was undertaken to unequivocally establish the stereochemistry. A perspective view of the molecular structure of one of the crystallographically independent molecules is shown in Fig. 1, confirming that the major adduct is in fact the *exo*-diastereoisomer, consistent with an earlier assignment.[11]

ROMP of **4** with *cis*-cyclooctene was catalysed by 2 mol% $[RuCl_2(PCy_3)_2({=}CHPh)]$ in chloroform at room temperature. Following polymerisation, the reaction was quenched with ethyl vinyl ether and the catalyst removed by extraction with an aqueous solution of tris(hydroxymethyl)phosphine, according to a protocol developed by Pederson *et al.*[12] The molecular weight of **5** determined by gel permeation chromatography (GPC) was measured to be 9100 Da (M_w), relative to polystyrene standards, in good agreement with the theoretical value based on complete consumption of monomer as confirmed by ^1H NMR spectroscopy. The polydispersity of 1.03 is also consistent with a narrow monomodal molecular weight distribution (Fig. 2). The ratio of pyrrolidinium bromide to cyclooctene incorporated into the polymer was determined to be 0.5 from elemental analysis, which corresponds to an x value of 50/3, based on the average molecular weight of **5**. Analysis of the polymer by ICP-OES revealed the ruthenium content to be less than 0.001 wt%. The thermal stability of the copolymer **5** was investigated by thermogravimetric analysis and differential scanning calorimetry. The TGA showed two main degradation stages (ESI†) and indicated that copolymer **5** was thermally stable up to 170 °C, which is above the reaction conditions required for the liquid phase catalysis.

The peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was selected for immobilisation because it is an efficient catalyst for alkene epoxidation and alcohol oxidation and as such was used to assess the relative merits of PIILP catalysis. Catalyst **6** was prepared by stoichiometric exchange of the bromide anions of **5** with $[PO_4\{WO(O_2)_2\}_4]^{3-}$, generated by hydrogen peroxide-mediated decomposition of the heteropolyacid $H_3PW_{12}O_{40}$;[13] the product precipitated as an insoluble white amorphous solid immediately upon mixing. Decomposition of heteropoly acid $H_3PW_{12}O_{40}$ into $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was confirmed by a signal at δ 2.8 ppm in the solid state ^{31}P NMR spectrum, which also showed the presence of several unidentified phosphorus-containing species previously observed by Hill and co-workers during their study on the formation, reactivity and stability of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (ESI†).[13f] Nitrogen sorption analysis of **6** gave a BET surface area of 42 $m^2\ g^{-1}$ and pore size distribution curves calculated by Barret–Joyner–Halenda method gave an average pore size of 8.3 nm and a pore volume of 0.15 $cm^3\ g^{-1}$. These values are consistent with similar polyoxometalate-based polyammonium cation hybrid mesoporous materials with surface areas of 27–51 $m^2\ g^{-1}$, albeit with a smaller pore size of 3.6 nm.[6] Analysis of **6** by transmission electron microscopy (TEM) showed that the polymer is granular in nature with small highly contrasting features of *ca.* <1 nm, corresponding to the peroxophosphotungstate, surrounded by the poorly contrasting cation-decorated co-polymer (Fig. 3a). ICP-OES analysis of **6** gave a tungsten content of 26.0 wt%, which is consistent with the proposed formulation.

The efficiency of **6** was investigated for the epoxidation of allylic alcohols and alkenes as these reactions have been catalysed by peroxophosphotungstate-based systems immobilised on

Table 1 Epoxidation of allylic alcohols and alkenes with hydrogen peroxide in acetonitrile catalysed by **6** and **7**[a]

Entry	Substrate	Catalyst	Time	Conversion[b,c]
1		**6**	4	>99 (94)
2		**7**	4	74 (66)
3		**6**	4	89 (81)
4		**7**	4	87 (74)
5		**6**	4	>99 (92)
6		**7**	4	94 (86)
7		**6**	4	96 (91)
8		**7**	4	97 (89)
9		**6**	12	88 (81)
10		**7**	12	82 (71)
11		**6**	4	98 (91)
12		**7**	4	74 (68)
13		**6**	4	89 (79)
14		**7**	4	80 (71)
15		**6**	4	81 (72)
16		**7**	4	98 (89)
17		**6**	5	76[d]
18		**7**	5	79[d]

[a] Reaction conditions: 0.5 mol% **6** or **7**, 1 mmol substrate, 2 mmol 35% H_2O_2, 3 mL MeCN, 50 °C. [b] Determined by GC analysis of the reaction mixture using decane as internal standard. Average of three runs. [c] Isolated yield in parenthesis. [d] Determined by ^{1}H NMR spectroscopy.

the surface of silica,[4] polymers and polycationic dendrimers,[5,8] as well as in ionic liquids.[14] Parallel catalyst testing was also undertaken with $[PO_4\{WO(O_2)_2\}_4][NEt_4]_3$ (**7**); full details are given in Table 1. Our initial evaluation focused on the epoxidation of *trans*-hex-2-en-1-ol by hydrogen peroxide using 0.5 mol % catalyst in acetonitrile at 50 °C and, under these conditions, **6** gave 99% conversion after 4 h compared with 74% for the **7**, over the same reaction time (entries 1 and 2). Table 1 shows that **6** also gave good to excellent conversions for the epoxidation of a range of allylic alcohols and alkenes and, encouragingly, in the majority of cases outperformed **7**. Epoxidation of 3,7-dimethyl-2,6-octadien-1-ol occurred with complete regioselectivity for the allylic alcohol to give the 2,3-epoxy alcohol as the sole product in good yield (entries 7 and 8). Although **6** was less effective for the epoxidation of homoallylic alcohols (entries 9 and 10), good conversions could be obtained over longer reactions times. Gratifyingly, the conversions obtained with **6**, for the epoxidation of cyclooctene, approach those recently achieved with 9- and 27-armed peroxometalate-cored dendrimers[5] as well as peroxometalate-based room temperature ionic liquids.[14b] Future work will systematically explore the efficiency of this PIILP catalyst as a function of polymer microstructure, ionic environment and porosity with the aim of optimising performance and broadening substrate scope.

Reasoning that a polymer-immobilised ionic liquid phase support should effectively retain the immobilised peroxophosphotungstate, catalyst reusability experiments were undertaken in order to assess the longevity of the catalyst and the potential for incorporation into a continuous flow process. The catalyst reusability was studied up to four cycles, by recycling the catalyst recovered after centrifugation and siphoning off the liquid phase at the end of each cycle. Recovered catalyst was used as such and no make-up quantity of fresh catalyst was added. The reusability data for **6** showed that the epoxidation of cyclooctene went to completion each time and the catalyst **6** recycled effectively with only a minor reduction (~6%) in reaction rate after each recycle (Fig. 4). Analysis of the solvent after filtration and recovery of the catalyst revealed that the tungsten content was too low to be detected by ICP-OES (*i.e.* <1 ppm), confirming that leaching was negligible. The reduction in conversion observed on successive recycles is thought to be due to attrition during filtration and recovery of the catalyst; this will be further investigated by performing scale-up recycle experiments to improve and quantify catalyst recovery and modifying the surface properties and ionic microenvironment to improve catalyst–surface interactions, substrate accessibility and efficiency. Interestingly, the TEM image of **6** recovered after the 4th recycle in the catalytic epoxidation of *cis*-cyclooctene (Fig. 3b) shows some aggregation of the peroxophosphotungstate; however, the solid state ^{31}P NMR spectrum of recycled catalyst **6** showed that the tetranuclear peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is stable, in agreement with earlier studies by Ishii *et al.* and Venturello *et al.*[13]

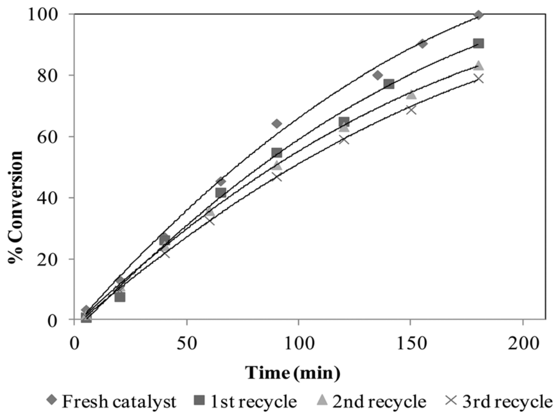


Fig. 4 Conversions with respect to time for the hydrogen peroxide-mediated epoxidation of *cis*-cyclooctene catalysed by **6**.

Conclusion

In conclusion, ROMP has been used to prepare a novel linear cation-decorated polymer based on a pyrrolidinium monomer and cyclooctene co-monomer. The derived peroxophosphotungstate polymer-immobilised ionic liquid phase catalyst is an efficient system for the epoxidation of allylic alcohols and alkenes and, encouragingly, the catalyst could be recovered in an operationally straightforward procedure and reused with only a minor reduction in performance. Future studies will aim to exploit ROMP as a tool for the controlled assembly of new highly tuneable support materials and to this end we are currently (i) exploring what factors influence catalyst performance with the aim of identifying an optimum catalyst–support combination for use in a continuous flow process, (ii) elucidating property–function relationships, (iii) establishing whether the polymer chain of the catalyst support has been epoxidised, (iv) investigating whether functional co-monomers can be incorporated into the polymer chain to modify chemo- and enantioselectivity, (v) developing novel architectures such as nanocapsules and polymeric micelles and (vi) extending the concept of PIILP catalysis to a wider range of transformations.

Experimental

Ring opening metathesis polymerisation of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide with *cis*-cyclooctene

A flame-dried three-neck round bottom flask under a nitrogen atmosphere was charged with chloroform (80 mL), *cis*-cyclooctene (3.0 mL, 23.0 mmol) and **4** (4.23 g, 11.7 mmol). To this was added a solution of $[RuCl_2(PCy_3)_2({=}CHPh)]$ (0.571 g, 0.694 mmol) in chloroform (*ca.* 10 mL) and the resulting mixture was heated at 40 °C and left to stir for 19 h. Upon completion the reaction was allowed to cool to room temperature, ethyl vinyl ether (0.69 mL, 7.0 mmol) added and the solution stirred for an additional hour. The polymer was precipitated by slowly adding the reaction mixture portion-wise to diethyl ether (*ca.* 600 mL) with vigorous stirring; after stirring for a further 60 min the polymer was isolated by filtration, using a sintered glass frit, washed with diethyl ether and dried to yield 5.2 g of a pale green solid. A solution of tris(hydroxymethyl)phosphine was prepared by degassing 2-propanol (90 mL) with nitrogen for 30 min prior to adding tetrakis(hydroxymethyl)phosphonium chloride (2.6 mL, 18 mmol). Potassium hydroxide (1.0 g, 18.0 mmol) was added slowly over 15 min to the vigorously stirred solution during which time a white precipitate formed. The mixture was allowed to stir for an additional 10 min and then added to a solution of the polymer in chloroform (*ca.* 100–150 mL). After heating at 60 °C for 19 h, NaBr (18.52 g, 180 mmol) was added and the mixture stirred for an additional 3 h at 60 °C. The mixture was then filtered, washed rigorously with distilled water (3 × 50 mL) and the resultant organic layer added dropwise to diethyl ether (*ca.* 500 mL) with vigorous stirring. After stirring for a minimum of 60 min the polymer was allowed to settle, isolated by filtration through a frit, washed with diethyl ether (2 × 50 mL) and dried under high vacuum to afford **5** as a buff brown solid in 61% yield (4.1 g). ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.52–7.78 (br, C_6H_5), 7.24–7.50 (br, C_6H_5), 5.14–5.52 (br,$=CH$), 3.41–4.11 (br, NCH_2Ph + NCH_2CMe), 2.17 (br, cyclopentane CH), 1.69–2.10 (br, cyclopentane CH_2 and CH and$=CHCH_2$), 1.05–1.41 (br, CH_3 and cyclopentane and alkyl CH_2); $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ): 133.4, 133.2, 130.6, 130.4, 129.9, 129.2, 128.9, 32.6, 29.8, 29.6, 29.2, 29.1, 27.2, 21.8; Anal. Calc for $C_{36}H_{56}NBr$: C, 74.20, H, 9.69, N, 2.40. Found: C, 73.82, H, 10.01, N, 2.35 (corresponding to a pyrrolidinium monomer content of 62.5 mol%, 1.72 mmol g^{-1}); GPC (average over 3 runs): $M_w = 9100$, $M_n = 8600$, PDI = 1.06.

Synthesis of polymer supported peroxophosphotungstate 6

A hydrogen peroxide solution (35% w/w, 9.7 mL, 100 mmol) was added to phosphotungstic acid (1.73 g, 0.6 mmol) dissolved in a minimum volume of water and stirred at room temperature for 30 min. After this time, pyridine (0.145 mL, 1.8 mmol) was added followed by a solution of 5 (0.877 g, 1.8 mmol) in the minimum volume of ethanol, which resulted in the immediate precipitation of an amorphous white solid. The mixture was cooled to 0 °C, filtered through a sintered glass frit and the precipitate washed with water (2 × 10 mL) and diethyl ether (3 × 75 mL) and dried under vacuum to afford 6 in 84% yield. FT-IR (KBr plates): $\tilde{\nu}$ = 1086, 1058, 1035 (P–O), 957 (W═O), 837 (O–O), 563, 535 $W(O_2)_{s,a}$; Anal. Calc for $C_{108}H_{168}N_3O_{24}PW_4$: N, 1.58; W, 27.66. Found: N, 1.46; W, 26.00.

General procedure for catalytic epoxidations

A Schlenk flask was charged with substrate (1.0 mmol), catalyst (2 mol% based on W) and acetonitrile (3 mL) and the resulting mixture heated at 50 °C with rapid stirring. The reaction was initiated by the addition of hydrogen peroxide (35% solution, 0.18 mL, 2 mmol) and stirred for the allocated time. After the reaction mixture had cooled to room temperature decane (0.195 mL, 1.0 mmol) was added and the resulting mixture was then diluted with diethyl ether (25 mL) and washed with water. The organic layer was separated, dried over magnesium sulphate, concentrated under reduced pressure and analysed by GC-MS to determine the conversion before being purified by column chromatography.

Acknowledgements

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