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Synthesis and application of novel catalytically active polymers containing 1,4,7-triazacyclononanes†

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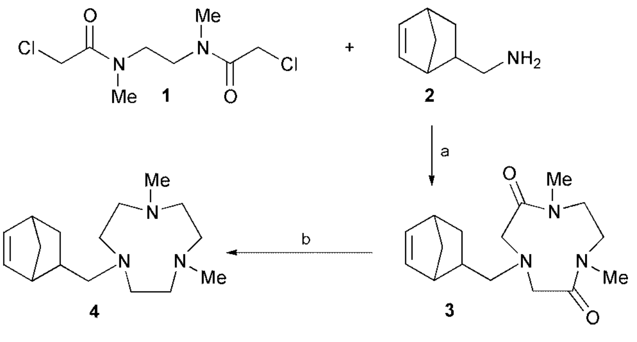
New polymers containing 1,4,7-triazacyclononanes have been synthesised by means of ring opening metathesis polymerisation (ROMP); their complexes with Mn(II) catalyse the oxidation of simple olefins by hydrogen peroxide.

The ongoing interest in environmentally benign processes for oxidations of simple organic molecules has led to the development of various catalytic systems for the activation of H_2O_2. Among these, manganese–triazacyclononane complexes have received considerable attention in recent years.[1] Simple protocols allow epoxidations to be performed in water–cosolvent mixtures using catalytic amounts of such complexes and hydrogen peroxide as stoichiometric oxidant. However, separation and recycling of the catalysts are still major challenges, and several strategies have already been investigated. For example, triazacyclononanes (TACNs) have been linked to silica affording heterogeneous systems, which can easily be recovered by filtration.[2] Alternatively, perfluorinated side chains were introduced onto the TACN in order to allow for fluorous biphasic catalysis (FBC).[3] Unfortunately, most of these approaches led to systems with reduced catalytic activity and lower product selectivity. Thus, a feasible immobilization strategy which allows maintenance of the positive attributes of the 'free' triazacyclononane–manganese system is still missing. In this work, we now present the synthesis of polymeric structures bearing a dense arrangement of 1,4,7-triazacyclononane moieties by application of ROMP.[4] With hydrogen peroxide as terminal oxidant manganese complexes of such polymeric ligands efficiently catalyse epoxidations of simple olefins exhibiting activities and selectivities which are comparable to those of the monomeric systems. Allylic and benzylic alcohols are also oxidised. In the case of conjugated alkenes, other oxidation products (*e.g.* diols) are formed as well.

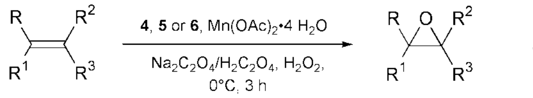
Monomer **4** containing a polymerisable norbornene‡ element and a 1,4,7-triazacyclonane unit was readily assembled from norbornenylmethylamine (**2**) following a well-established bis(chloroacetamide) cyclisation–reduction sequence (Scheme 1).[5] Purification *via* column chromatography or high-vacuum distillation afforded **4** in 15% overall yield.



Scheme 1 Synthesis of the monomer **4**. *Reagents and conditions*: (a) Na_2CO_3, LiBr, CH_3CN, reflux, 12 h; (b) $LiAlH_4$, THF, reflux, 6 h.

Attempted polymerisation of monomer **4** with Grubbs's catalyst[6] failed, probably due to interference of the multiple amine groups present in the molecule. Protonated **4** gave polycationic polymers, which, unfortunately, only showed negligible catalytic activity in the epoxidation of olefins when combined with manganese salts and hydrogen peroxide. To our delight, Schrock's molybdenum based catalyst[7] reacted with the free triamine **4** rapidly and efficiently, allowing the preparation of desired polymer **5** in quantitative yield (Scheme 2). In these preliminary studies, 5 mol% of the catalyst was employed in all runs, setting the number of triazacyclononane units per molecule (n) at about 20. The terminal ends of the polymer were capped by treatment of the reaction mixture with pivaldehyde after complete consumption of the monomer. Diimide mediated hydrogenation afforded saturated polymer **6** (with a degree of hydrogenation of *ca.* 86%) in 70% yield.

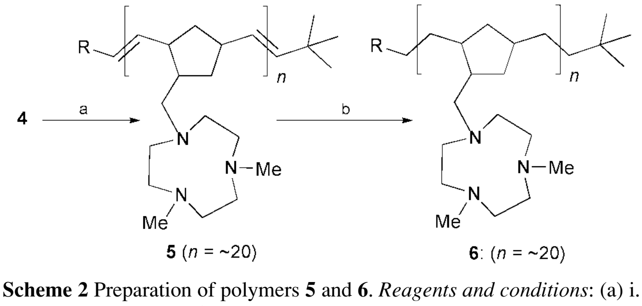
The performance of manganese catalysts derived from polymers **5** and **6** in olefin oxidations with hydrogen peroxide was investigated under the conditions indicated in eqn. (1).§



(1)

In all runs, 1 mol% of active catalyst (based on 3.7 mmol TACN units per g of polymer) formed *in situ* from Mn$(OAc)_2 \cdot 4H_2O$ and **4**, **5**, or **6** was employed. Both the ligand and the manganese complexes were soluble in aqueous acetone–methanol–H_2O_2 mixtures. The presence of sodium oxalate as co-ligand proved essential for the efficiency of the reaction.[8] Noteworthy is the fact that the conversion of the substrates was negligible in the absence of the triazacyclononane-containing polymers. The most significant results of this study are summarised in Table 1.

The performance of the polymeric systems in catalysing the oxidation reactions was in most cases comparable or even superior to that of the corresponding monomeric azacycle. Simple aromatic olefins were converted efficiently to the corresponding epoxides (entries 1–4). In the cases of α-methylstyrene and indene notable amounts of diols were



Scheme 2 Preparation of polymers **5** and **6**. *Reagents and conditions*: (a) i. Schrock's catalyst (5 mol%), toluene, RT, 4 h; ii. Pivaldehyde; (b) *p*-tolylsulfonylhydrazide, NaOH, di(ethylene glycol) methyl ether, 120–130 °C, 1.5 h.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b1/b105560g/

Table 1 Oxidation of organic substrates with manganese catalysts prepared from **4** and polymeric 1,4,7-triazacyclononanes **5** and **6**

Entry	Substrate	Monomer **4**: Conv. (%) (Epoxide selectivity (%)[a])	Polymer **5** Conv. (%) (Epoxide selectivity (%)[a])	Polymer **6** Conv. (%) (Epoxide selectivity (%)[a])
1	Styrene	75 (87)	88 (91)	78 (92)
2	β-Methylstyrene	43 (93)	48 (83)	40 (83)
3	α-Methylstyrene	88 (86)	92 (62)[b]	86 (69)
4	Indene	98 (63)[c]	80 (64)[c]	70 (61)
5	Cyclohexene	100 (83)	100 (90)	94 (92)
6	Cyclooctene	32 (87)	41 (85)	49 (92)
7	Hex-1-ene	58 (100)	66 (100)	50 (95)
8	(*E*)-Hex-3-ene	58 (71)	29 (100)	23 (100)
9	(*Z*)-Hex-3-ene	100 (71)[d]	100 (91)[e,f]	83 (90)[e]
10	Methyl acrylate	4 (100)	12 (83)	7 (100)
11	Methyl cinnamate	16 (100)	23 (91)	18 (94)
12	3-Phenylpropenol[g]	100 (72)	76 (50)	54 (55)
13	1-Hydroxymethylcyclohexene[h]	96 (73)	80 (67)	68 (75)
14	Benzyl alcohol[i]	73	69	52
15	2-Phenylethanol	41	31	21

[a] Calculated as the ratio of epoxide yield and conversion. [b] A notable amount (11–27%) of the corresponding diol is produced. Other byproducts include benzophenone and 2-phenylpropionaldehyde. [c] The main byproduct is indan-2-one (10–24%). A notable quantity (6–11%) of the corresponding *cis*-diol is also produced. [d] + 17% of the corresponding *trans*-epoxide. [e] + 8% of the corresponding *trans*-epoxide. [f] 0.03 M oxalic buffer was employed. [g] A considerable amount (21–27%) of the corresponding α,β-unsaturated aldehyde is formed in this reaction. [h] Notable amounts (13–17%) of the corresponding α,β-unsaturated aldehyde are formed in this reaction. [i] The main products are benzaldehyde (18–29%) and benzoic acid (22–55%).

formed. Most probably this result is due to a subsequent epoxide hydrolysis under these reaction conditions.¶ Aliphatic alkenes were also epoxidised. In particular, internal (*Z*) systems reacted more effectively than terminal or (*E*) olefins (entries 5–9). In the case of (*Z*)-hex-3-ene, a significant amount of *trans*-epoxide was produced. α,β-Unsaturated carbonyl compounds showed poor reactivity (entries 10, 11). Hydroxy groups in the allylic or benzylic position were oxidised. In the case of allylic alcohols, both the epoxy alcohol and the corresponding α,β-unsaturated aldehyde were formed (entries 12, 13), with the epoxidation being the main reaction pathway. The two products did not undergo further transformations. The possibility of converting alcohols to conjugated systems was demonstrated by the oxidation of benzyl alcohol to benzaldehyde and benzoic acid (entry 14) as compared to the relatively less efficient transformation of 2-phenylethanol, which gave the corresponding aldehyde in low yield (7–11% of the reaction mixture) (entry 15). Finally, the procedure described herein was successfully performed of a 100 mmol scale with styrene as substrate, and no variation in conversion or selectivity was observed.

In conclusion, the possibility of generating polymeric systems with a high density of 1,4,7-triazacyclononane units by ROMP has been demonstrated. The corresponding manganese complexes are catalytically active in oxidation reactions with hydrogen peroxide as terminal oxidant. Currently, we are studying alternative polymeric systems based on the model presented with improved characteristics regarding catalyst stability and recovery.

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Notes and references

‡ The IUPAC name for norbornene is bicyclo[2.2.1]hept-2-ene.

§ General experimental procedure: a solution of 1 mmol of substrate in acetone (GC quality, 1 mL) is cooled to 0–2 °C and treated with the ligand (for **4**: 2.7 mg in 48 μL of MeOH, 0.01 mmol; for **5** or **6**: 2.7 mg in 48 μL of MeOH, 0.5 μmol) and $Mn(OAc)_2\cdot 4\,H_2O$ (2.5 mg in 141 μL of H_2O, 0.01 mmol). The mixture is stirred for 15 min. Oxalic buffer (0.15 M, 0.133 mL, 0.02 mmol) is added, followed within 1–2 min by H_2O_2 (30%, 0.4 mL, 4 mmol). After stirring for 1.5 h at 0–2 °C, another aliquot of H_2O_2 is added (0.2 mL, 2 mmol). After a reaction time of 2.5–3 h, the excess oxidant is destroyed by adding a small quantity of MnO_2, the reaction mixture is diluted with approx. 2 mL of CH_2Cl_2 and the organic phase is separated and analysed by gas-chromatography (see ESI).

¶ Samples of pure α-methylstyrene oxide were converted to the corresponding diol when exposed to the reaction conditions.

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