Epoxidation of cyclohexene with polymethacrylate-based peroxotungstic catalysts

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Abstract

Amino and ammonium groups have been introduced into polyglycidylmethacrylate (PGMA) resins by reaction of trimethylamine either by opening the epoxide ring of PGMA or by reaction with methyl iodide followed by amination. The aminoalky derivatives were phosphorylated to afford grafted phosphotriamides; when loaded with tungsten species in their peroxo form, these polymeric carriers exhibited excellent properties as catalysts for the epoxidation of cyclohexene with hydrogen peroxide. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Several tungstic anions in the free form, complexed or polycondensed, are known to catalyse the epoxidation of alkenes with hydrogen peroxide as an external oxidant [1–6]. For the purpose of recycling and to get tungsten-free products and effluents, some of these catalysts have been previously immobilized as ionic or neutral species on polystyrene-based resins [7–9].

We reported recently epoxidations with polystyrene-grafted phosphorous ligands as polymeric complexing agents for ionic or neutral peroxotungstic species [10].

To check the influence of the hydrophilic–hydrophobic balance inside the polymeric matrices and the effects on the kinetics, we have now experimented with other polymeric carriers in the epoxidation of cyclohexene as a typical substrate.

The occurrence of a variety of possible side-reactions also presented an opportunity to check the selectivity of the supported catalysts. Besides the expected epoxide, cyclohexen-2-ol and cyclohexen-2-one may form through radical oxidation at the allylic position; diol and hydroxy-hydroperoxide may also appear by hydrolysis or perhydrolysis, respectively and cleavage of the ring may subsequently occur [11–13] (Fig. 1).

We describe here the preparation and the use of polymethacrylate (PMA)-based phosphotri-

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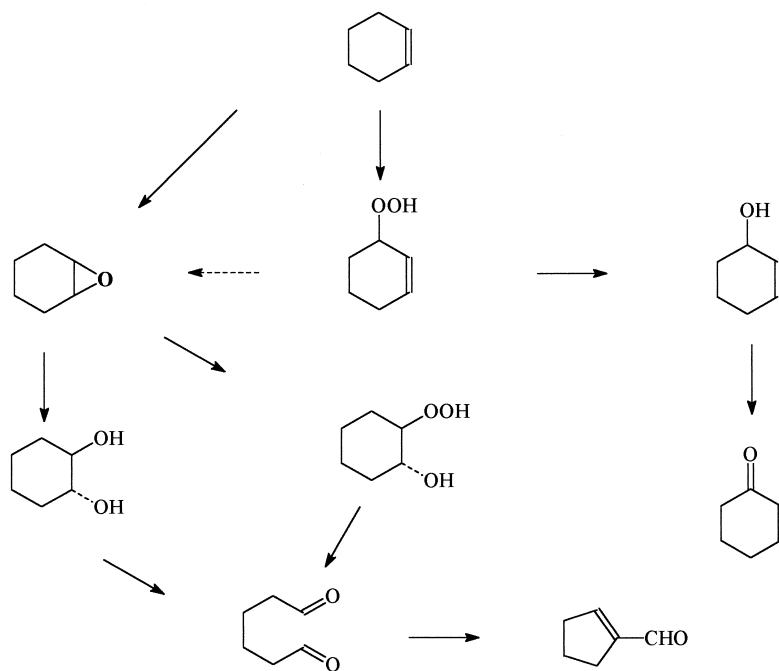
Fig. 1. Epoxidation of cyclohexene and side reactions.

amides and anion exchange resins obtained through the ring-opening of the oxirane function in polyglycidylmethacrylate (PGMA) copolymers.

Preformed peroxotungstic species were immobilized on these carriers and the epoxidation of cyclohexene investigated.

2. Experimental

2.1. Copolymers of glycidyl methacrylate 1

The polymerisations were performed in a 2 l double-walled glass reactor fitted with a anchor-shaped stirrer, a condenser and an external heater. Water (900 ml) and polyvinylpyrrolidone (9 g) were stirred and heated at 70°C for 2 h under a nitrogen atmosphere. The monomers were introduced in one portion: glycidyl methacrylate (49 ml, 359 mmol), butyl methacrylate (49 ml, 359 mmol) and ethyleneg-

lycol dimethacrylate (2 ml, 10 mmol). The stirring was regulated at 500 rpm and polymerisation was initiated with AIBN (azobisisobutyronitrile, 1.03 g). After 1 h, the stirring was reduced to 250 rpm and 1 h later, the temperature was raised to 80°C. This was maintained for 6 additional hours under a nitrogen stream. After cooling, the beads were filtered, crushed and washed in a Soxhlet for 5 h with acetone.

One oxirane unit corresponds to the composition-derived formula $C_{15.6}H_{24.8}O_{5.22}$ (MW = 294.1); elemental analysis: calc. % C 63.27, H 8.45, O 28.28; found C 63.0, H 8.4, O 28.3; oxirane group titration [14], calc. 3.40 meq/g, found 3.10; FTIR (KBr, cm^{-1}) 3001, 2953 ν(CH in CH$_2$), 1732 ν(C=O), 1488, 1452 δ(CH), 1274 and 1270 ν(C–O epoxide and ester), 1149 ν(C–O ester), 749 δ (epoxide ring).

Macroporous copolymers (42 molar% of EGDMA) were made in the presence of a 1/1 mixture of cyclohexanol/dodecanol as a diluent in a equal volume of that of the monomers. FTIR (KBr, cm^{-1}) 2992, 2951 ν(C–H), 1730
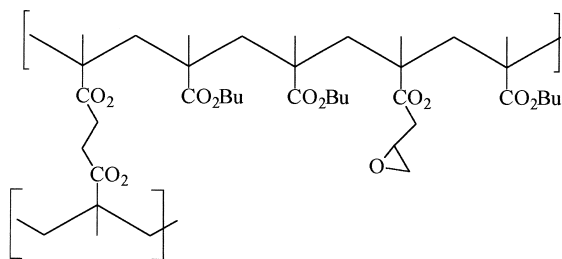
Fig. 2. Glycidyl methacrylate copolymers.

ν(C=O), 1480 and 1452 δ(C–H in O–CH$_2$), 1260 ν(C–O epoxide), 1160 ν(C–O ester).

2.2. 2-Hydroxy-3-dimethylaminopropyl PMA 2

Dioxane (40 ml), a 40% aqueous solution of dimethylamine (69 ml) and copolymer **1** (2.35 g) were introduced to a 250 ml round-bottomed flask and the mixture was heated at 60°C for 24 h under gentle stirring. The resin was water-washed over a frit until the effluent was pH neutral, then rinsed with two volumes of acetone and vacuum dried at 60°C.

Elemental analysis for the macroporous resins **2a**: calculated formula from one starting oxirane unit: C$_{11.8}$H$_{16.8}$O$_{4.93}$ (MW = 191); calc. % C 59.1 H 8.02 O 28.47, found C 55.3 H 8.25 O 30.0; FTIR (KBr, cm^{-1}) 3437 ν(OH, H bounded), 1730 ν(C=O), 1466 δ(C–H in O–CH$_2$), 1160 ν(C–O ester).

Resin **2b** was obtained similarly with pure dibutylamine.

2.3. 2-Hydroxypropyl-3-trialkylammonium halide PMA 3

In a 250-ml round-bottomed flask fitted with a magnetic stirrer, a condenser and a moisture trap, resin **2** (3 g) was suspended in dioxane (60 ml); then 10 eq. of an alkyl halide were added and the mixture heated for 4 h (at 60°C with methyl iodide, at 80°C with propyl bromide or 1-chloro-2-ethanol). The resin was filtered off, transferred into a glass column and rinsed with

a NaCl solution (1 M, 500 ml) to remove Br$^-$ and I$^-$ anions. The resin was finally water-washed until no trace of Cl$^-$ was detected in the washings. The resins were stored moist and analytical samples were washed with dioxane and methylene chloride before drying.

The quaternisations were found to be quantitative in all cases as shown by elemental analyses (N/Cl $\cong$ 1). FTIR (KBr, cm^{-1}), 2992–2952 ν(C–H), 1726–1730 ν(C=O), 1478–1483 δ(C–H), 1154–1160 (νC–O ester and alcohol).

2.4. 2-Methoxy-3-iodopropyl PMA 4b

In a 250-ml round-bottomed flask fitted with a condenser and a moisture trap, resin **1b** (20 g, 68 meq oxirane) was allowed to swell for 30 min in dry DMF (150 ml); then methyl iodide (21.2 ml, 340 mmol, fivefold excess) and tetrapropylammonium iodide (1.06 g, 3.4 mmol, 5 molar%) were added. The mixture was gently stirred and heated at 65°C for 60 h.

The resin was collected and methanol-washed in a Soxhlet for 4 h; the product was pure enough for amination reaction. Analytical samples were further washed with methylene chloride; elemental analyses: calc. % C 39.83 I 33.4, found C 44.76 I 27.15 (81% transformation). FTIR (KBr, cm^{-1}), 1733 ν(C=O), 1472 δ_{asym}(C–H O–Me), 1456 δ_{sym} (C–H C–OMe), 1264 ν(C–N), 1152 ν(C–O), 472–546 ν(C–I).

2.5. 2-Methoxy-3-methylaminopropyl PMA 5

Resin **4** (20 g, 40 mmol) was allowed to swell for 30 min in dimethoxymethane (''meth-

Table 1
Composition of PGMA copolymers

Ref.	BMA %	MMA %	GMA %	EGDMA %	mmol oxirane/g
1a	–	–	58	42[a]	4.2
1b	45	–	53	1.7	3.4
1c	74.7	–	22.8	2.5	2
1d	–	43.3	55.4	1.3	3.6

[a] Macroporous resin.

$$(PMA){-}CO_2CH_2{-}CH{-}CH_2 \xrightarrow{\text{RRNH}} (PMA){-}CO_2CH_2{-}CH{-}CH_2NR_2 \xrightarrow{\text{R'X}} (PMA){-}CO_2CH_2{-}CH{-}CH_2NR_2R^+ \;\; X^-$$

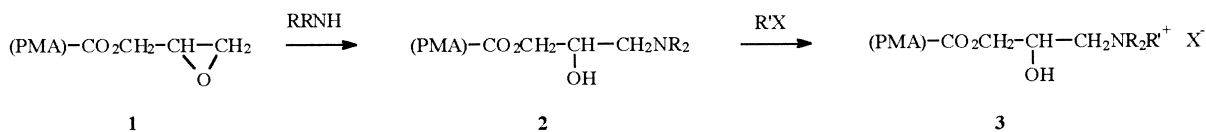   **1**   **2**   **3**

Fig. 3. PMA based anion-exchange resins.

ylal'', 100 ml) then a 35% aqueous solution of methylamine (100 ml, 850 mmol) was added, and the mixture was then stirred and heated at 50°C for 60 h.

The resin was filtered, washed in a column with NaOH (1 N, 200 ml) with water until neutral and then sequentially with methanol (150 ml), dioxane (70 ml), methylene chloride (50 ml) and finally dried at 60°C overnight.

Elemental analyses of resins **5a** (with MMA) and **5b** (with BMA) showed 3.4–4.7% of the initial iodine left and 85–99% of conversion of epoxide to amine; FTIR (KBr, cm^{-1}), 1732 ν(C=O), 1486 δ(C–H), 1271ν(C–N), 1158 ν(C–O).

2.6. PMMA-supported PMPA 6

A three-necked flask was fitted with a condenser and a dropping funnel and dry DMF (100 ml) was introduced. The flask was flushed with nitrogen; pentane-washed sodium hydride (0.48 g, 11.9 mmol, from the 60% oil suspension) was introduced and, after complete dispersion, resin **5** (7.92 mm eq.) was added; the suspension was heated under gentle stirring at 60°C for 3 h. The flask was allowed to cool to room temperature and a solution of tetramethyl phosphorodiamidic chloride (2 g, 11.9 mmol) in

DMF (5 m)L was added dropwise; the mixture was heated again at 60°C for 40 h.

The final resin was filtered, methanol-washed in a Soxhlet, and rinsed with methylene chloride. The analytical data are reported in Table 5; FTIR (KBr, cm^{-1}) 1267 ν(P=O), 993 ν(P–N).

2.7. PMMA-supported PMPA-WO$_5$ complexes 7

PMMA resin **6** (1.15 meq) in a conical flask was soaked overnight with shaking in a solution of peroxotungstic acid (3 ml, 2.4 meq W) in dioxane (20 ml). The beads were filtered and washed with methanol until neutral then rinsed with dioxane and methylene chloride. Drying was performed for 24 h at 50°C (never higher due to risks of decomposition of the peroxo species in the dry state). The analytical data are reported in Table 5; FTIR (KBr, cm^{-1}) 965 ν(W=O), 625 ν_{asym}(W–O–O), 550 ν_{sym}(W–O–O).

2.8. PMMA-supported ammonium peroxotungstates 8

Resin **3** (10 ml) in a glass column was slowly washed with a fivefold excess of WO$_5$ equivalents in the form of a 0.1 N aqueous solution of NaHW$_2$O$_{11}$; the resin was washed with water

Table 2
PMA-based quaternary ammonium resins **3**

Starting PGMA	Amine R'$_2$NH	meq N/g (DF %) in resins **2**	Alkylating agent	Resins **3** (N/X ratio)	meq N$^+$/g
1a	R' =CH$_3$	2.7 (87) **2a**	ICH$_3$	**3a** (0.94)	2.53
1a	R' =CH$_3$	**2a**	BrC$_3$H$_7$	**3b** (0.94)	1.94
1a	R' =CH$_3$	**2a**	ClC$_2$H$_4$OH	**3c** (0.92)	2.24
1b	R' =C$_4$H$_9$	2.8 (94) **2b**	ICH$_3$	**3d** (1.0)	2.0
1b	R' =C$_4$H$_9$	2.1 (88) **2c**	BrC$_4$H$_9$	**3e** (1.1)	1.50

$(PMA)-CO_2CH_2-CH-CH_2 \quad \xrightarrow{\quad Cl^- \quad} \quad (PMA)-CO_2CH_2-CH-CH_2Cl \quad \xrightarrow{\quad Me_3NH^+ \quad} \quad (PMA)-CO_2CH_2-CH-CH_2NMe_3^+$
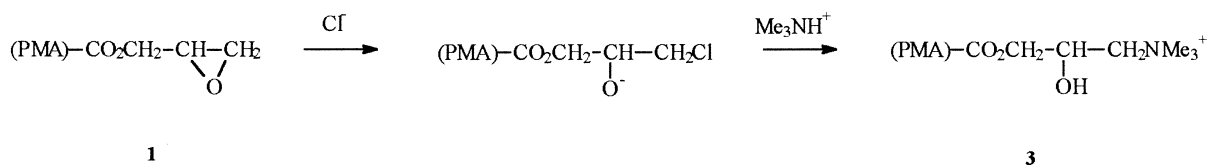
1 $\qquad\qquad\qquad\qquad\qquad$ **3**

Fig. 4. Direct access to β-hydrolylated PMA based anion-exchange resins.

then rinsed and dried as above. Resin **8a′** was obtained with a solution of $H_2W_2O_{11}$ and resins **8g** and **8h** with solutions of the relevant salts [3,15]; the analytical data are reported in Table 6. FTIR (KBr, cm^{-1}) 1737 and 1714 ν(C=O), 960 ν(W=O), 869 ν(O–O), 666 ν_{sym}(W < O–O), 543 ν_{sym}(W < O–O).

2.9. Polystyrene-supported ammonium peroxotungstates 10

Gel-type chloromethylated polystyrene beads with increasing chlorine capacity are available from Eastman-Kodak (0.7 meq Cl/g), Aldrich (1.1), BioRad (1.35) and Fluka (2.2). In a round-bottomed flask equipped with a reflux condenser, 50 meq of choromethylated resins were swelled in 50 ml of dimethoxymethane for 1 h at 35°C, then 200 mmol of trimethylamine (from a 40% aqueous solution) were added and the mixture heated under gentle stirring for 2 h at 40°C. The condenser was replaced by a distillation still and the temperature increased to 60°C; after the distillation, the cold resin was poured in 100 ml of 1 M HCl, stirred for several minutes and finally water-washed until the neutrality of the filtrate was achieved.

A sample of resin **9** was put in a small glass column, washed with a few milliliters of acetonitrile; a solution of 2 g of $(NBu_4)_2$ $C_6H_5-PO_3(WO_5)_2$ [15] in 10 ml acetonitrile was percolated through a bed of the resin; after washing with the solvent, the resin **10** was vacuum-dried overnight. The tungsten contents are given in Table 8.

2.10. General method of epoxidation

Epoxidations were performed at 70°C in a 100 ml thermostated glass reactor fitted with a condenser, a dropping funnel and a gas burette (to measure O_2 which may result from the decomposition of hydrogen peroxide); cylohexene (296 mmol), decane (5 mmol as an internal standard), dioxane (30 ml) and the catalyst (0.18 meq W, 0.6 molar%) were introduced and the system was swept by a nitrogen stream when heating. When the temperature was stabilised, the nitrogen flow was stopped and 1 ml (27.2 mmol) of 65% hydrogen peroxide was added dropwise.

2.11. Monitoring

The reference compounds, epoxycyclohexane, 2-cyclohenen-1-ol, 2-cyclohexen-1-one and *n*-decane were commercially available Fluka pure compounds and were used as such. The reaction was monitored on a Carlo Erba Fractovap GLC apparatus fitted with a JW-DB1 silicon column and a FID detector with the following operating conditions: oven 70°C, N_2 flow 5 ml/min, retention times, epoxide mn, enol, enone, decane mn, diol mn. At the end of the

Table 3
Direct synthesis of quaternary ammonium PMA-resins **3**

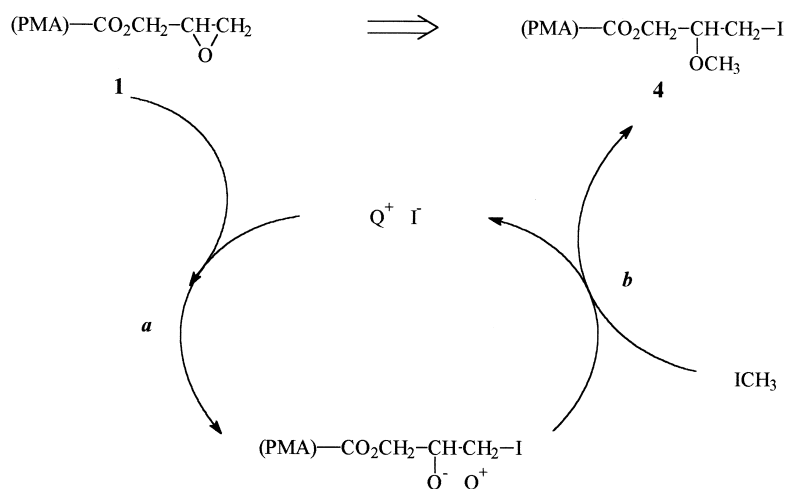| PGMA resin	Molar composition	Exchange capacity (N%)
1e (gel-type)	MMA (55.3%) GMA (43.4%) EGMA (1.3%)	1.93 meq N/g (2.72)
LS6 (macroporous)	GMA (83%) DVB (17%)	2.93 meq N/g (4.13)

Fig. 5. Iodomethylation of PGMA copolymers.

reaction and after cooling, the reaction mixture was adjusted in a volumetric flask and the unreacted hydrogen peroxide was titrated by iodometry so as to get the conversion.

3. Results and discussion

3.1. Preparation of the PMA polymeric ligands

3.1.1. Copolymers of GMA

Gel-type and macroporous glycidylmethacrylate (GMA)-based polymers were obtained by copolymerisation with methyl- or butylmethacrylate (MMA and BMA, respectively) as comonomers and with divinylbenzene (DVB) or ethyleneglycol-dimethacrylate (EGDMA) as cross-linking agents.

Suspension polymerisation were performed with 2 up to 46% of EGDMA to get gel-type or macroporous polymer beads. The latter were obtained with cyclohexanol/dodecanol mixtures as porogenic solvents (Fig. 2).

The analytical data for these PMA copolymers are reported in Table 1.

3.1.2. Amination and quaternisation

For the immobilisation of peroxotungstic species, several quaternary ammonium deriva-

tives **3** were obtained in two-step reaction similar to that reported by Svec et al. [16] involving the opening of the oxirane ring with secondary amines followed by quaternisation of the intermediate tertiary amines **2** (Fig. 3).

The amination reaction always proceeded with > 90% conversion but required a large excess of amine. The quaternisation reactions were complete (Table 2).

We have also found that some of these quaternary ammonium derivatives can be obtained *directly* by a one-pot reaction when using tertiary amine hydrochlorides (Fig. 4).

The postulated pathway involves the ring-opening of the oxirane by the chloride anion to give a chloro-alcolate which deprotonates the tertiary amine, releasing the free amine for the quaternisation step. The reactions were straightforward and essentially quantitative yields of

Table 4
Iodoalkylated PMA resins **4**

Starting PGMA	Iodoalkylated PMA resins	Capacity meq I/g (I %)	DF %
1a	**4a**	2.14 (27.2)	83
1b	**4b**	2.13 (27.1)	82
1c	**4c**	1.1 (13.5)	85
1d	**4d**	1.55 (19.74)	98

$(PA)-CO_2CH_2-CH\cdot CH_2-I$ $\longrightarrow$ $(PA)-CO_2CH_2-CH\cdot CH_2-NHCH_3$ $\longrightarrow$ (PA)—...

4   **5**   **6**
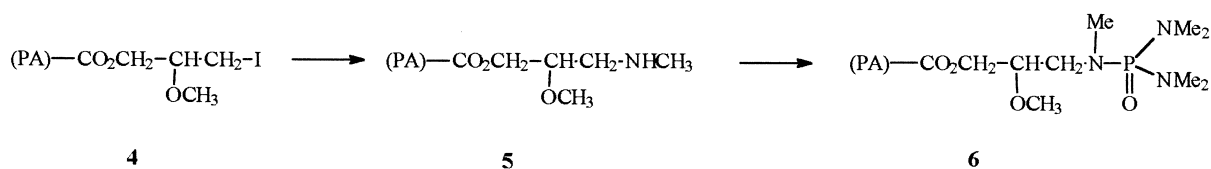
Fig. 6. Phosphotriamide derivatives of PGMA copolymers.

the ammonium ion function from oxirane were obtained. The results are reported in Table 3.

It should be mentioned here that the three substituents $R^1R^2R^3$ in the quaternary ammonium group are introduced at the same time through the tertiary amine $NR^1R^2R^3$. As a common feature, all these quaternary ammonium derivatives have a β-OH group between the polymeric chain and the ammonium group.

During the sequence **2** → **3** some additional cross-linking may occur though the same side reaction of the intermediate alcolate as reported in Fig. 4 (vide infra); this may explain discrepancies between the original oxirane content of the resins and the final capacity of quaternary ammonium groups.

Anyhow, this approach is very original as most of the commercially available PMA-based anion exchange resins result from the transamidation of methylmethacrylate copolymers with 2-(dimethylamino)ethylamine followed by a quaternisation step.

3.1.3. Iodomethylation

Most of the functionalised polystyrenes are derived from gel-type or macroporous chloromethylated derivatives [17] after reaction with nucleophilic species. The analogous halo-

genated PMA species are not available as starting material.

We therefore devised a new pathway to obtain halogenated PMA from PGMA copolymers which results from the formal addition of methyl iodide to the oxirane ring in the presence of quaternary ammonium halide as catalyst (Fig. 5).

The postulated mechanism relies on the ring-opening by nucleophilic attack of the halide [18], which first affords the iodoalcolate (step *a*) and then the methyl ether forms through a Williamson reaction with methyl iodide (step *b*). The iodide anion, which is displaced, can react again with another oxirane.

With gel-type polymers, some additional cross-linking may also occur after step *a* when a vicinal oxirane in the polymer is opened through a nucleophilic attack of the alcolate.

Several iodoalkylated polymers **4** were prepared in this way from PGMA copolymers **1** and the relevant data are reported in Table 4.

This new iodomethylation procedure affords a family of ω-iodoalkylated polymers **4** which can be considered as the polyacrylate analogues of Merrifield resins. Their use as electrophilic polymers in several other functionalisation reactions is currently under investigation.

Table 5
PMA-supported PMPA ligands **6** and complexes **7**

Iodoalkyl-PMA	PMA-supported HMPA	N/P ratio	meq P/g (P%)	Peroxotungstic-loaded resins **7** (meq W/g)	P/W ratio
4a	**6a**	4.68	0.59 (1.84)	**7a** (1.10)	0.36
4b	**6b**	4.97	0.38 (0.98)	**7b** (0.08)	4.61
4c	**6c**	4.15	0.58 (1.81)	**7c** (0.90)	0.50
4d	**6d**	2.92	0.57 (1.78)	**7d** (0.70)	0.72

$$6 \xrightarrow{\text{H}_2\text{W}_2\text{O}_{11}} (PA)-CO_2CH_2\text{-}CH\text{-}CH_2\text{N}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}\overset{\displaystyle NMe_2}{\underset{\displaystyle WO_5}{\overset{\displaystyle NMe_2}{\diagdown}}}$$
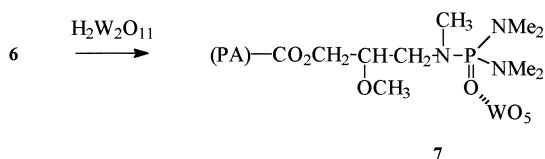
7

Fig. 7. Peroxotungstic species immobilised on phosphotriamide derivatives of PGMA.

3.1.4. Phosphorylation

As HMPA has been shown to be a good complexing ligand for WO_5 [19], we described previously some polystyrene-supported HMPA complexed with peroxotungstic species as catalyts [10] for alkene epoxidation. The PMA-supported analogues **6** were expected to show improved activities.

The phosphoramide ligand was introduced by the reaction of tetramethyl phosphorodiamidic chloride with the amino resins **5**, the latter being obtained after treatment of the iodo intermediate **4** with an aqueous solution of methylamine (Fig. 6).

The final capacities of the phosphorylated PMA resins are given in Table 5.

The formation of phosphotriamide groups should give an N/P atomic ratio = 3. With the exception of resin **6d**, in practice the other samples exhibited values > 3 which indicates the presence of free methylamino groups remaining as a result of uncomplete phosphorylation.

3.1.5. Complexation or exchange with peroxotungstic acid

The PMPA resins were swollen in dioxane and impregnated with a solution of peroxotungstic acid $H_2W_2O_{11}$. This afforded the expected neutral species **7** (Fig. 7).

In some cases, the elemental analytical data showed the presence of polyperoxotungstic species when the P/W atomic ratio is < 1 (Table 5). The typical IR band of complexed HMPT was found at 1267 cm^{-1} for $\nu(P=O)$ [19].

The PMA–ammonium resins were exchanged with the $HW_2O_{11}^-$ anion from a dioxane–water solution of tetrabutylammonium hydrogen peroxotungstate $Bu_4NHW_2O_{11}$. The structure and the content of the tungsten-loaded resins are given in Table 6.

For the sake of comparison, two commercially available polyacrylate-based macroporous resins Amberlite IRA958 and Lewatit AP247A

Table 6
Peroxotungstic supported on PMA-based ammonium resins[a]

PMA-based ammonium	Structure	Capacity (meq W/g)	N/W
2a → 8a′	$PMA-CO_2CH_2CH(OH)CH_2-NHMe_2^{+}$ [b]	2.15	0.60
3a → 8a	$PMA-CO_2CH_2CH(OH)CH_2-NMe_3^{+}$	1.70	0.90
3b → 8b	$PMA-CO_2CH_2CH(OH)CH_2-NMe_2Pr^{+}$	1.75	0.75
3c → 8c	$PMA-CO_2CH_2CH(OH)CH_2-NMe_2(C_2H_4OH)^{+}$	1.55	0.70
3d → 8d	$PMA-CO_2CH_2CH(OH)CH_2-NMe_3^{+}$	1.45	1.0
3e → 8e	$PMA-CO_2CH_2CH(OH)CH_2-NBu_3^{+}$	1.30	0.90
IRA958[c] → **8f**	$PMA-CO_2C_2H_4-NMe_3^{+}$	1.70	3.0
IRA958 → **8g**	$PMA-CO_2C_2H_4-NMe_3^{+}$ $PW_4O_{22}^{3-}$ [d]	1.90	1.10
IRA958 → **8h**	$PMA-CO_2C_2H_4-NMe_3^{+}$ $C_6H_5-PO_3(WO_5)_2^{2-}$ [e]	2.10	0.80
AP247A[f] → **8i**	$PMA-CO_2C_2H_4-NMe_3^{+}$	2.40	1.37

[a] With $HW_2O_{11}^-$ anion unless quoted.
[b] Non-quaternised tertiary amine.
[c] Macroporous polyacrylate Amberlite from Rohm & Haas.
[d] With the $PW_4O_{22}^{3-}$ anion [3].
[e] With the $C_6H_5-PO_3(WO_5)_2^{2-}$ anion [5,15].
[f] Macroporous polyacrylate Lewatit from Bayer.

$$(PS){-}CH_2Cl \longrightarrow (PS){-}CH_2NMe_3^+ \; Cl^- \longrightarrow \left[(PS){-}CH_2NMe_3^+ \right]_2 \; C_6H_5PO_3(WO_5)_2^{--}$$

9   **10**
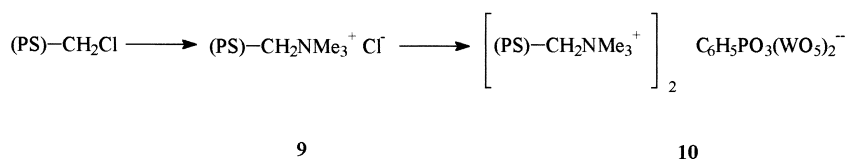
Fig. 8. Peroxotungstic species immobilised on polystyrene-based quaternary ammonium resins.

were examined as well. Though their exact composition is unknown, they were exchanged with $HW_2O_{11}^-$ and with the complex phospho- and phosphonoperoxo tungstate anions $PW_4O_{22}^{3-}$ and $C_6H_5{-}PO_3(WO_5)_2^{2-}$ as already described [3,15]. These anions exhibit excellent catalytic properties in homogenous solution.

Though the elemental analytical data (N/W ratio) showed that the exchange was not complete, the tungsten contents of the final catalysts ranged from 0.08 up to 2.36 meq W/g. This allowed the study of the influence of the loading on the efficiency of the catalysts. It should be noted that the commercial resins IRA958 and AP247A are designed to have a high capacity of ammonium groups, and so not surprisingly exhibit higher contents of tungsten.

3.2. Preparation of polystyrene-supported peroxotungstic ammonium salts

These polystyrene-supported catalysts **10** were obtained from a series of Merrifield-type chloromethylated polystyrene resins of increasing chlorine capacity; they were first treated with trimethylamine so as to get the quaternary ammonium species **9** and then exchanged by percolation with a acetonitrile solution of the ammonium peroxotungstate $(NBu_4)_2 \; C_6H_5{-}PO_3(WO_5)_2$ [15] (Fig. 8).

3.3. Epoxidation of cyclohexene

Cyclohexene was chosen as a model substrate for screening the catalysts. The experiments were performed with variable amounts of polymer so as to adjust the level of tungsten to a constant value 0.5% molar vs. the substrate. The liquid phase was made homogeneous by adding dioxane to the cyclohexene/hydrogen peroxide mixture. The reaction was monitored by GLC and the final hydrogen peroxide content was determined by iodometry; then, the conversion included the spontaneous and catalysed decomposition *and* the effective oxygen transfers to the substrate; oxygen and allylic oxidation

Table 7
Epoxidation of cyclohexene with peroxotungstic species supported on PMA ammonium resins **8**

Catalyst	Conv. H_2O_2 (%)	Yield epoxide (%)	By-products yield (%)[a]			Time	Capacity (meq W/g)	Initial TOF[b]
			Diol	Allyl.	O_2			
8a′	95	38	62	0	0	50 min	2.15	515
8a	71	84	0	11	5	4 h	1.70	33
8b	89	65	11	16	8	4 h	1.75	34
8c	82	68	24	9	0	4 h	1.55	46
8d	76	49	0	22	30	4 h	1.45	41
8e	99	54	46	0	0	3 h	1.30	197
8f	72	22	0	33	45	21 h	1.70	11
8g	67	42	0	37	20	22 h	1.90	22
8h	76	48	3	30	15	22 h	2.10	27
8i	72	18	0	0	82	4 h	2.40	6

[a] 1,2-Cyclohexane diol, 2-cylohexenol and 2-cyclohexenone, O_2 from decomposition of H_2O_2.
[b] Units: mmol epoxide/mmol W/h.

Table 8
Epoxidation of cyclohexene with polystyrene-supported peroxotungstic anion[a]

Catalyst	meq W/g	Time (h)	H_2O_2 conv. (%)	Yield epoxide (%)	TOF
10a	0.11	1.75	92	89	135
10b	0.52	0.75	97	88	193
10c	0.72	1.25	94	86	123
10d	1.1	4.5	83	73	28
Soluble[b]		1	97	97	154

[a] $C_6H_5-PO_3(WO_5)_2^{2-}$.
[b] $(NBu_4)_2 C_6H_5-PO_3(WO_5)_2$, see Ref. [15].

derivatives were considered as by-products. The yields of epoxide are referred to the amount of hydrogen peroxide introduced, the turnover frequencies (TOF) are the initial ones.

The results with PMA-based ammonium salts are reported in Table 7.

Catalyst **8a′** is a simple tertiary ammonium salt and exhibits an exceptional catalytic efficiency (TOF = 515) but the protonated amine > NH + is too acidic as shown by the extensive formation of diol; then, the corresponding quaternary ammonium salts **8a** and **8d**, which are neutral, are very selective as no diol at all is formed, but this is at the expense of the reactivity which dropped significantly. This is a general phenomena found with tungsten-based catalyst where a balance must be found for the pH of the medium: acidity induces both the reactiv-

ity of the salt *and* the hydrolysis of the epoxide which was formed. Increased bulkiness (**8b**) or local hydrophilicity (**8c**) around the ammonium ion seems to promote some hydrolysis, the reasons for which are not clear yet.

The catalysts **8e–8i** were made from commercial resins; they induced decomposition of hydrogen peroxide or afforded significant levels of enol and enone as a result of oxidation at the allylic position, irrespective of the peroxotungstic anion being used; this might be due to the high loading density with the tungsten-based complex. The high capacity of these polymers (which was required for their industrial uses as ion exchangers) make the environment of the catalytic sites very polar, thus less prone for the diffusion of the apolar alkene; this may explain the prolonged reaction time required to get significant chemical yields.

The effect of increasing polarity inside the polymer beads, around the catalytic site, was examined by as study performed with the same $C_6H_5-PO_3(WO_5)_2^{2-}$ peroxoanion immobilized on a series of polystyrene carriers containing increasing amounts of quaternary ammonium groups.

For the same amount of tungsten involved, when increasing the capacity of the resin from 0.11 to 1.1 meq W/g, the yields and the conversion of hydrogen peroxide remain quite simi-
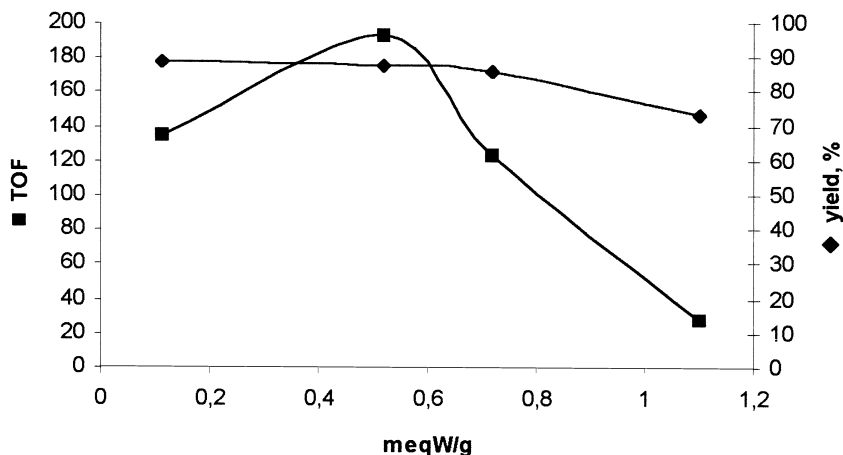

Fig. 9. Influence of the capacity of the resins on the reactivity.

Table 9
Epoxidation of cyclohexene with peroxotungstic species supported on PMA–HMPA resins **7**

Catalyst	H_2O_2 conv. (%)	Epoxide selec. (%)	By-products (%)			Time	Capacity (meq W/g)	TOF[b]
			Diol	Allyl.[a]	O_2			
7a	87	77	13	0	10	45 min	1.10	405
7b	88	86	0	1	12	10 min	0.08	1235
7c	94	91	0	0	8	45 min	0.90	229
7d	89	81	0	0	16	10 min	0.70	1176
Soluble[c]	93	57	28	0	14	5 h	–	74

[a] 2-Cylohexenol and 2-cyclohexenone.
[b] Units: mmol epoxide/mmol W/h.
[c] WO_5, HMPA, H_2O according to Ref. [19].

lar as reported in Table 8, but the reaction time required to get the same yield is not the same. The corresponding TOF values show a maximum as shown in Fig. 9.

This maximum TOF value is obtained with a resin containing about 0.5 meq W/g; that would correspond to a local polarity which provides such a hydrophilic–hydrophobic balance that the non-polar alkene and the very polar hydrogen peroxide can diffuse at a similar rate towards the catalytic sites. It should be noted also that this maximum TOF value is somewhat higher than what was given by the corresponding soluble ammonium salt: here the polarity around the metal is optimised vs. what occurs in homogeneous solution.

Below 0.4 meq W/g, the polymer is very little polar and not suitable for the diffusion of H_2O_2; in the contrary, above 0.8 meq W/g, the resin is much too polar for a good diffusion of the alkene. This subtle equilibra should be determined for each type of polymeric carrier.

In all cases, the metal salt remained tightly bound in the resins, as shown by the low value of W (< 2 ppm) found in the supernatant reaction mixture after reaction.

The last series of experiments were performed with the PMA-based phosphoramides **6** as macroligands, as shown by the data in Table 9 which were found even more remakable.

The gel-type resins **7b**, **7c** and **7d** were found extremely selective towards epoxide formation as no diol nor allylic oxidation products were formed; *TOF values above 1000* were obtained;

and the macroporous resin **7a** was even better than the ionic gel-type **8a** mentioned above.

Also particularly interesting here is the comparison with the soluble catalyst analogue HMPT,WO_5 which was found to have a rather low activity (TOF = 75) and to be somewhat acidic.

This is the first report of immobilized homogeneous metal complex catalysts where both the activity and selectivity are significantly higher (by a factor 17) than the soluble analogues.

This exceptional behaviour seems to be accounted for by the lipophilic–hydrophilic balance inside the polymeric beads which behave as microreactors, as mentioned above. The interior polar structure is compatible with both the polar hydrogen peroxide *and* the non-polar alkene, thus allowing good diffusion of all reactants and product. Such a favourable situation cannot readily occur in homogeneous solution.

4. Conclusions

We found aminophosphorylated PMA as remarkable ligands for peroxotungstic species in the selective epoxidation of alkenes with hydrogen peroxide as no cleavage products formed [20]. Since no leakage of metal was observed (less than 2 ppm W) these PMA-based phosphoramides appear very appropriate for further studies including: (i) improving the hydrophilic–hydrophobic balance with even more appropriate methacrylate monomer compositions; (ii) re-

peated recyclings of the same sample of catalyst using the ''tea-bag'' technique [21,22]; (iii) the use of the polymers in triphasic conditions: alkene + aqueous H_2O_2 + polymeric beads; and (iv) experiments with a series of other alkenes.

Acknowledgements

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