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Catalytic Epoxidation of Olefins with *t*-Butyl Hydroperoxide in the Presence of Polymer-supported Vanadium(V) and Molybdenum(VI) Complexes

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Oxovanadium(V) and oxomolybdenum(VI) ions have been incorporated into cross-linked polystyrene resins functionalized with iminodiacetic acid or diethylenetriamine derivatives. The polymer complexes have been used as catalysts in the epoxidation of olefins with *t*-butyl hydroperoxide. Vanadium(V) complexes promote epoxidation of allylic alcohols in a highly regioselective manner, *e.g.*, 2,3-epoxide has been preferentially obtained in 98% selectivity from (*E*)-geraniol at 80 °C. The catalytic activity of the vanadium(V) complexes is generally higher than that of the molybdenum(VI) complexes in the epoxidation of allylic alcohols whereas an opposed trend holds for the epoxidation of cyclohexene. Life time of catalysts have been examined by repeated use of the complexes in the epoxidation of (*E*)-geraniol at 80 °C in benzene. Approximately 15—25% of vanadium has been leaked out of the polymer beads on five time recycles leading to the decrease in the yield of 2,3-epoxide from initial value of 98% to 95—93%. Neither appreciable loss of metal nor reduction of catalytic activity has been observed in the molybdenum complex systems over five runs.

It is widely known that complexes of oxometal ions such as vanadium, molybdenum, and tungsten catalyze the epoxidation of olefins with alkyl hydroperoxides.[1—7] Recently anchoring of catalytically active transition metal complexes onto a polymer matrix received considerable attention[8,9] due to their potential advantages in practical synthesis, *i.e.*, i) the catalyst is easily separated from the reaction solution by filtration or centrifugation, ii) the recovered catalyst can be used repeatedly.

Several studies have been carried out on the catalytic epoxidation of olefins by polymer-anchored metal complexes.[10—13] However the functional groups so far used as metal-ion-binding unit were mostly monodentate and bidentate ligands, which often suffer from the disadvantage of the metal ion leaking from the polymer support. Accordingly a more stable metal-polymer linkage is required to avoid such leaking of metal ion into the reaction solution.

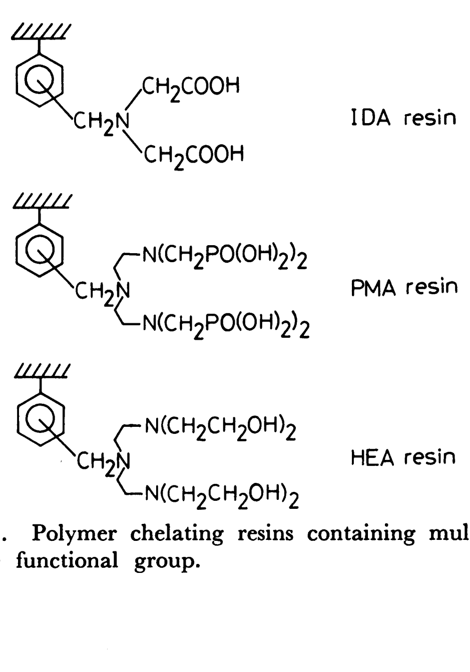

Fig. 1. Polymer chelating resins containing multidentate functional group.

Recently we have reported that the cross-linked polystyrene resins with a functional group having bis(phosphonomethyl)amino (PMA) and bis(2-hydroxyethyl)amino (HEA) moieties (Fig. 1) readily form metal complexes with oxovanadium(V) and oxomolybdenum(VI) ions in aqueous solution.[14] These polymer complexes were found to catalyze the epoxidation of (*E*)-geraniol with *t*-butyl hydroperoxide (*t*-BuOOH) without significant loss of the metal ion.[15] This is the full detailed description of the work including the preparation of the polymer complex catalysts, and the epoxidation of allylic alcohols and cyclohexene.

Experimental

Materials. Microreticular (Gel) and macroreticular (MR) types of polystyrene resins containing iminodiacetic acid (IDA) moieties are commercial products, *i.e.*, Dowex A-1 (Gel type, 25—50 mesh) and Lewatit-OC-1048 (MR-type, 25—50 mesh). The polymer matrices used for the preparation of PMA and HEA resins were Gel-type styrene-2%-divinylbenzene copolymer (from Kodac Co, 200—400 mesh) and MR-type styrene-10%-divinylbenzene copolymer (from Mitsubishi Chemical Co., 60—100 mesh). The surface area and mean pore radius of the MR-type resin were 7.3 m^2 g^{-1} and 720 Å, respectively.

Preparation of the Chelating Resins. Both Gel- and MR-types of polystyrene beads were chloromethylated,[16] and then functionalized with diethylenetriamine (dien) to give a dien-resin in which diethylenetriamine is linked to the polymer uniquely through the secondary amino nitrogen.[17] The dien-resin was used as the starting material for the preparation of the PMA and HEA resins.

PMA Resin: To a refluxed mixture of dien-resin (Gel-type, 15 g), phosphorous acid (33 g) and 6 M HCl (80 cm^3, M=mol dm^{-3}) was added dropwise 37% of aqueous formaldehyde solution (64 cm^3) in the course of 2 h. The reaction mixture was kept at refluxing temperature for an additional 3 h. The resin was filtered, washed with water, ethanol and then diethyl ether, and dried *in vacuo* at 50 °C. Yield: 25.3 g.

HEA Resin: The Gel-type of dien–resin (11 g) was stirred with aqueous ethylene oxide (9.6 g in 100 cm^3) for 3 h under ice cooling. After standing overnight at room temperature, the resin was filtered, washed throughly with water, ethanol and diethyl ether, and then dried *in vacuo* at 50 °C. Yield: 19.5 g.

Functionalization of the MR-type polystyrene resin was performed under similar conditions to those for the Gel-type of PMA and HEA resins.

Preparation of Polymer Complexes: Polymer complexes were generally prepared by the following procedures: One gram of dry resin was shaken with 10 mM of aqueous $NaVO_3$ or K_2MoO_4 solution (1000 cm^3) at pH about 4 for 24 h. The concentration of the remaining metal ion in the solution was analyzed by atomic absorption spectrometry to determine the amount of metal adsorbed on the resin. The polymer beads were filtered, washed throughly with distilled water, ethanol, diethyl ether, and then dried *in vacuo* at 50 °C.

Epoxidation of Olefins: A typical procedure for the epoxidation of allylic alcohols is as follows: In a 50 cm^3 round-bottomed flask equipped with a reflux condenser was placed a polymer complex containing 0.2—0.3 mmol of metal, 30 cm^3 of benzene, (*E*)-geraniol (4.0 g, 26 mmol) and 70% of aqueous *t*-BuOOH (4.0 g, 31 mmol). The reaction mixture was heated at 80 °C with stirring. The reaction was monitored by TLC. After the reaction was completed, the polymer beads were filtered off, and the filtrate acetylated by the published method[3] prior to the product analysis. The reaction conversion of allylic alcohol and the distribution of the products were analyzed on a GLC (2% OV-17 on Uniport HP, 80—100 mesh: 16 ft×1/8 in.) using methyl stearate as an internal standard. The geometry of the epoxide isomers was confirmed by ^{1}H NMR spectroscopy. Epoxidation of cyclohexene was carried out under conditions similar to those for the epoxidation of the allylic alcohols. The reaction solution was analyzed on a GLC (15% PEG-20M on Uniport S, 60—80 mesh, 16 ft×1/8 in.) using toluene as an internal standard.

Lifetime of the Catalysts: The polymer complexes were recovered by filtration at the end of the epoxidation of (*E*)-geraniol. After washing with benzene, the complexes were used in successive runs under identical conditions. The conversion and the selectivity were determined after each run as described above. In order to determine the amount of metal ion which leaked into the reaction solution, the polymer catalyst was removed by filtration. The filtrate was evaporated and extracted twice with 0.5 M HCl. The metal ion in the extract was determined by atomic absorption.

Catalytic Decomposition of t*-BuOOH*: Decomposition of *t*-BuOOH was monitored by iodometry in the absence of a substrate. To a mixture of the polymer complex (100 mg) and benzene (30 cm^3) was added 70% of aqueous *t*-BuOOH (4.0 g) and the whole heated at 80 °C with stirring. Small portions of the sample (1 cm^3) were withdrawn at appropriate intervals and titrated iodometrically according to the published method.[18]

Measurements: ^{1}H NMR spectra were measured with a JEOL FX-100 spectrometer in chloroform-*d* with TMS as an internal standard. The metal ion concentration was determined with a Shimadzu atomic absorption/flame photometer Model AA-610S. GLC-analysis was performed on a Varian Model 3700 gas-chromatograph equipped with an electron digital integrator Varian Model CDS-111.

Results

Polymer Catalysts. Analytical data and the amounts of the functional group contained in one gram of dry resin are shown in Table 1. The ligand contents of Gel- and MR-type resins (PMA and HEA) do not differ much from each other, indicating that the functionalization proceeds to a similar extent, irrespective of the type of polymer support. However the physical form of the Gel-type resin is affected by the solvent while the MR-type resin has only minor shrinking and swelling properties. Metal ions were incorporated into the polymer ligands by treating the

Table 1. Analytical data of polymer chelating resins and the maximum adsorption capacity for V(V) and Mo(VI)

Chelating Resin	Analytical Data	Ligand Capacity[a]	Ads. Capacity/(mmol/g-resin)[b]	
	N(%)	mmol/g-resin	V	Mo
Gel-IDA	6.27	4.46	1.7	1.1
MR-IDA	3.64	2.60	1.4	2.0
Gel-PMA	6.53	1.55	3.2	3.3
MR-PMA	5.54	1.32	3.3	4.0
Gel-HEA	7.32	1.74	3.1	3.2
MR-HEA	7.43	1.77	4.0	4.0

a) Calculated from the actual nitrogen content: Ligand capacity (mmol/g-resin) is estimated by $\frac{\%N}{14n}$, where %N=nitrogen in product, and n=number of nitrogen atoms in the ligand.[29] b) The amount of metal adsorbed on one gram of dry resin.

resins with aqueous Mo(VI) or V(V) solution at pH *ca.* 4.0, conditions under which the amounts of metal adsorbed are maximal. The maximum adsorption capacities of the present resins for Mo(VI) and V(V) are also given in Table 1. The amounts of metal adsorbed on one gram of PMA and HEA resins always exceed the ligand contents while those on IDA resins do not.

Epoxidation of Allylic Alcohols. The results of epoxidation of allylic alcohols are summarized in Table 2. (*E*)-Geraniol was epoxidized preferentially at the olefinic site close to the hydroxyl group regardless of the metal ion, the functional group or the type of polymer matrix. The following general features were observed in the present reactions: i) The conversion of (*E*)-geraniol and the selectivity toward the formation of 2,3-epoxide by vanadium catalysts are generally higher than those by the molybdenum complex systems. ii) Apparently complexes with the MR-type polymer matrix undergo epoxidation at a much faster rate than the corresponding complexes of the Gel-type polymer. iii) The catalytic activities are almost independent of the type of functional group. iv) The epoxidation rate is retarded by addition of an excess amount of *t*-butyl alcohol (*t*-BuOH). Vanadium complexes epoxidize (*E*)-geraniol almost quantitatively and the selectivity is remarkably high (≈98%). The reaction conversion and the selectivity are comparable to those observed with homogeneous $VO(acac)_2$ (acac=acetylacetonato) when MR-vanadium complexes were employed. The epoxidation of 2-cyclohexen-1-ol and linalool was carried out in a similar manner to that of (*E*)-geraniol in the presence of vanadium complexes of MR-type resin. The reaction of these secondary and tertiary alcohols required much longer reaction times and resulted in lower conversion.

The time-course plots of the epoxidation of (*E*)-geraniol by vanadium catalysts are illustrated in Fig. 2. The reaction at 80 °C is facile in the initial stage and in most of the cases 80% conversion was attained within 30 min. Although it takes longer reaction time, the epoxidation proceeds under moderate temperature (20 °C) by use of MR-vanadium catalysts. The vanadium complexes of IDA and PMA resins accomplished 80—90% conversion in 8 h whereas HEA resin required much longer induction periods.

Epoxidation of Cyclohexene. Epoxidation of cyclohexene with *t*-BuOOH (cyclohexene/*t*-BuOOH=1) was carried out using vanadium(V) and molybdenum(VI) complexes of MR-type resins. Table 3 shows the conversion of cyclohexene and the selectivity toward the formation of cyclohexene oxide after a 24 h reaction period. In contrast to allylic alcohols, the epoxidation of a simple olefin catalyzed

TABLE 2. CATALYTIC EPOXIDATION OF ALLYLIC ALCOHOLS WITH POLYMER-SUPPORTED METAL COMPLEXES[a]

Substrate	Catalyst		Time/h	Conversion/%[b]	Selectivity/%[c]
	Resin	Metal			
(*E*)-Geraniol	Gel-IDA	V	24	100	98
		Mo	24	87	90
	MR-IDA	V	1	100	98
		Mo	24	96	82
	Gel-PMA	V	4	100	98
		Mo	24	89	81
	MR-PMA	V	1	100	98
		Mo	24	94	78
	Gel-HEA	V	4	100	98
		Mo	24	93	80
	MR-HEA	V	1.5	100	98
		Mo	24	98	71
		$VO(acac)_2$	0.5	100	98
2-Cyclo-hexen-1-ol	MR-IDA	V	6	89	87
	MR-PMA	V	24	53	88
	MR-HEA	V	24	100	90
Linalool	MR-IDA	V	24	70	53
	MR-PMA	V	24	48	53
	MR-HEA	V	24	70	55

a) Reaction was carried out at 80 °C. b) Conversion of allylic alcohol. c) Percentage of β,γ-epoxy alcohol in the products.

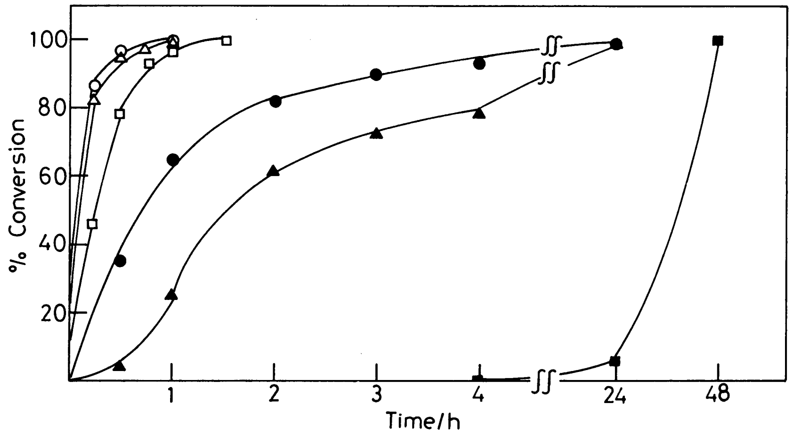

Fig. 2. Time-conversion profile of (E)-geraniol by polymer-anchored vanadium(V) complexes —○—: MR-IDA resin at 80 °C, —●—: MR-IDA resin at 20 °C, —△—: MR-PMA resin at 80 °C, —▲—: MR-PMA resin at 20 °C, —□—: MR-HEA resin at 80 °C, —■—: MR-HEA resin at 20 °C.

Table 3. Epoxidation of cyclohexene with polymer-supported metal catalyst[a)]

Catalyst		Conversion/%[b)]	Selectivity/%[c)]
Resin	Metal		
MR-IDA	V	59	6
	Mo	77	59
MR-PMA	V	29	5
	Mo	88	55
MR-HEA	V	76	4
	Mo	86	54

a) Epoxidation was carried out at 80 °C for 24 h. b) Conversion of cyclohexene. c) Percentage of cyclohexene oxide in the products.

Table 4. Metal-catalyzed decomposition of t-BuOOH (in benzene at 80 °C)

Catalyst		$t_{1/2}$(min)
Resin	Metal	
MR-IDA	V	210
	Mo	$\gg$15,000
MR-PMA	V	90
	Mo	$\gg$15,000
MR-HEA	V	90
	Mo	$\gg$15,000

by molybdenum gave a higher conversion and better selectivity than the reaction by vanadium complexes. The vanadium catalyzed reactions generally gave several by-products involving polymerized compounds.

Lifetime of Catalysts. The lifetimes of the catalysts (MR-resins) were examined by their repeated use in the epoxidation of (E)-geraniol. The amount of metal ion leaked into the solution was determined for each run. Approximately 75% of the vanadium remained on MR-IDA and MR-HEA resins while more than 85% of the metal was still retained on the MR-PMA resin after five runs. The yield of 2,3-epoxide decreased only slightly, *i.e.*, the initial value of 98% decreased to 95—93% after fivefold recycling. In most cases notable change in selectivity has not been observed. Leakage of the metal ion does not take place in the absence of substrate and t-BuOOH. Neither appreciable loss of metal nor reduction of catalytic activity was observed in the molybdenum complex systems after five runs.

Catalytic Decomposition of t*-BuOOH.* The rates of consumption of t-BuOOH by the polymer complexes in the absence of substrate have been monitored by iodometry. Half-lives ($t_{1/2}$) of the reactions are given in Table 4. Obviously vanadium complexes remarkably facilitate the decomposition of t-BuOOH while those by molybdenum complexes are very slow.

Discussion

The major advantage of polymer-anchored catalysts over their homogeneous counterparts is the ease of recovering and recycling of the catalysts. So far bidentate ligands such as ethylenediamine,[10)] acetylacetonato,[10,12)] and dithiocarbamato[13)] have been used as the polymer-metal (M=V(IV), Mo(V)) binding unit and the catalytic epoxidation of olefins has been carried out using the polymer complexes. However significant leakage of metal ion from the polymers inevitably took place during epoxidation, leading to a rapid lowering of the catalytic activity upon repeated use. Our catalyst systems, by contrast, are relatively long-lived. The catalytic activities after five runs are essentially the same as those of the first run irrespective of the catalysts used. The polymer–metal bond in these complexes appears to be very durable toward the dissociation of the metal ion under the given catalytic conditions. It has been pointed out that the rate of dissociation of a chelated complex decreases significantly as the dentate number of the ligand increases.[19] This trend was exemplified by the studies on acid hydrolysis of a number of Mo(V) complexes.[20,21] The enhanced stability of the present complexes may be attributed to the increasing dentate number of the immobilized ligands.

Iminodiacetic acid (IDA) which is the functional group of the IDA resin acts as a tridentate ligand and is known to form 1:1 (ligand:metal) complexes with Mo(VI) and V(V).[22–24] The facial tridentate coordination of IDA group to the trioxomolybdenum(VI) was proposed on the basis of the ^{1}H-NMR study of the IDA–Mo(VI) complex[23] and confirmed in the solid state for a 2:1 complex $Na_4(MoO_3)_2(edta)\cdot 8H_2O$ (H_4edta=ethylenediaminetetraacetic acid).[25] The PMA and HEA resins formally contain two sets of tridentate ligands, bis(phosphonomethyl)amino and bis(2-hydroxyethyl)amino moieties, respectively. The maximum amount of metal ion adsorbed on PMA and HEA resins is much higher than the estimated amount of ligand contained in one gram of dry resin. It seems that each of the tridentate ligand having one nitrogen and two oxygens as the donating atoms forms 1:1 complexes with Mo(VI) and V(V) in a similar fashion to those for IDA and EDTA complexes. The coordination of the hydroxyl arms onto Mo(VI) has been demonstrated by ^{13}C-NMR study of the Mo(VI) complex with *N,N,N′,N′*-tetrakis(2-hydroxyethyl)ethylenediamine.[14] The remaining coordination sites in the octahedral complexes are generally occupied with oxo ligands (or water) which can be replaced by the substrate or oxidizing agent in the epoxidation reaction. The higher durability of the PMA–V(V) complex toward metal dissociation suggests stronger coordination of the phosphonomethyl groups than that of the acetate or hydroxyl group.

As has been claimed earlier in the homogeneous catalyst systems[2,26] the high regioselectivity in the epoxidation of allylic alcohols can be interpreted by a mechanism in which coordination of the hydroxyl group of the substrate and *t*-BuOOH to the metal ion at neighbouring position is involved as the key intermediate. The fixed geometry of the allylic alcohols by the formation of such ternary complex results in preferential transfer of oxygen to an olefinic site close to the hydroxyl group. This may be supported by the observation that the rate of epoxidation is retarded in the presence of a large amount of *t*-BuOH which can compete with the substrate for coordination to the active center. With allylic alcohols vanadium complexes always gave a faster rate and better selectivity than the molybdenum complexes. A similar trend has been observed in the homogeneous catalyst system and has been attributed to the stronger coordination of hydroxyl group to vanadium.[2] In practice, the retardation by *t*-BuOH is more serious with vanadium complexes than with molybdenum complexes under similar reaction conditions.

Catalysts anchored on an MR-type resin always showed kinetic properties superior to those supported on a Gel-type resin. The MR-type resin has actual pores forming numerous channels which allow facile diffusion of the substrate into the polymer matrix.[27,28] On the other hand, the tight polymer network of the Gel-type resin may interfere with a smooth transfer of substrate to the active center.

Both vanadium and molybdenum complexes catalyze the decomposition of *t*-BuOOH to give peroxyl radicals.[4,6] Therefore the epoxidation of olefins catalyzed by these metal complexes involves competing with the metal-catalyzed decomposition of *t*-BuOOH. The vanadium-catalyzed decomposition of *t*-BuOOH is remarkably facile in the absence of a substrate, while in the presence of allylic alcohols, the epoxidation proceeds preferentially. An intramolecular oxygen transfer from peroxovanadium(V) complex to allylic alcohol seems to take place at a much faster rate than the decomposition of the peroxide when the olefins is fixed to metal through a functional group. On the contrary, the epoxidation of cyclohexene gave an extremely poor yield of epoxides indicating that the decomposition reaction takes place prior to the efficient oxygen transfer to the substrate. For the nonfunctionalized olefin the opportunity to form the stable ternary complex might be limited. Radicals produced by the homolytic decomposition of peroxide must be responsible for the formation of many kinds of byproducts. Reactions involving such peroxyl radicals would be less remarkable in the molybdenum-catalyzed epoxidation since the rate of decomposition of *t*-BuOOH is significantly slow.

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