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POLYMER-ANCHORED VANADIUM(V) AND MOLYBDENUM(VI) CATALYSTS FOR THE REGIOSELECTIVE EPOXIDATION OF (E)-GERANIOL WITH *t*-BUTYL HYDROPEROXIDE

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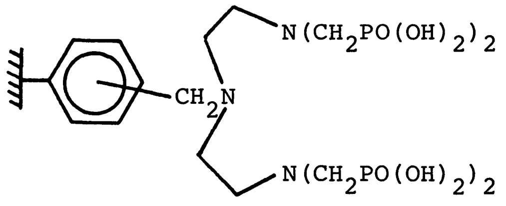
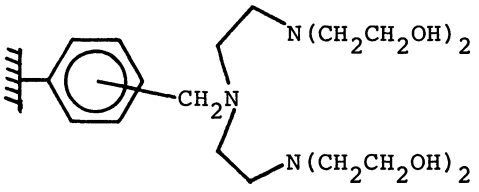
The reaction of (E)-geraniol with *t*-BuOOH in the presence of polymer-anchored V^{V} or Mo^{VI} complexes gave 2,3-epoxygeraniol in high yields. The conversion and the selectivity by the MR-type polymer catalysts containing V^{V} were comparable to those given by homogeneous catalyst based on $VO(acac)_2$. The present catalysts can be used repeatedly without causing significant decrease in catalytic activity.

Vanadium and molybdenum complexes are known to catalyze the epoxidation of allylic alcohols in highly regioselective manner.[1,2] Recently anchoring of transition metal catalysts received a considerable attention[3-6] due to their potential advantages for the practical synthesis, i.e., i) catalyst can be separated from the reaction system simply by filtration, ii) the recovered catalyst can be used repeatedly. So far little is known on the regioselective epoxidation of allylic alcohols with *t*-butyl hydroperoxide (*t*-BuOOH) by heterogenized metal complexes. We have synthesized the chelating polymer resins containing bis(phosphonomethyl)-amino (PMA) and bis(2-hydroxyethyl)amino (HEA) moiety, which can form complexes with oxo-vanadium(V) and oxo-molybdenum(VI) ions.[7] In this paper we describe the epoxidation of (E)-geraniol with *t*-BuOOH by the polymer-anchored oxo-metal complexes.

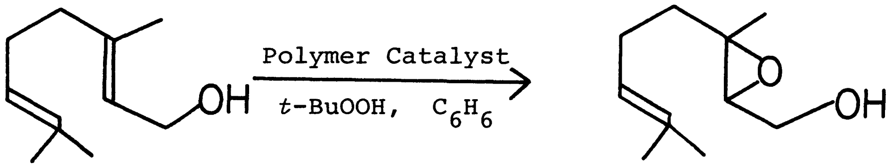


(PMA)-resin



(HEA)-resin

The polymer matrices of the present resins are microreticular (Gel-type) styrene-2%-divinylbenzene and macroreticular (MR-type) styrene-10%-divinylbenzene copolymer beads with 200-400 and 60-100 mesh, respectively.$^{8)}$ The PMA and HEA resins were prepared according to the method reported previously.$^{7)}$ The polymer catalysts were generally prepared by the following procedure: One gram of dry resin was shaken with 10 mM (M=mol dm^{-3}) of aqueous $NaVO_3$ or K_2MoO_4 solution (1 dm^3) at pH ranging 3 to 4 for 24 h. The polymer beads were filtered, washed with water, ethanol, diethyl ether, and then dried under reduced pressure at 50 °C. The amount of metal bound to the polymer was determined by atomic absorption spectroscopy.$^{9)}$ The epoxidation of (E)-geraniol was carried out as follows: A mixture of polymer catalyst, benzene (30 cm^3), (E)-geraniol (4.0 g, 26 mmol), and 70% of aqueous *t*-BuOOH (4.0 g, 31 mmol) was stirred at desired temperature. The reaction was monitored by TLC. After the reaction was completed, the polymer beads were filtered off, and the filtrate was acetylated prior to product analysis.$^{2)}$ The reaction conversion and the distribution of the products were determined by GLPC (2% OV-17) using methyl stearate as an internal standard. The geometry of the isomers of epoxides was confirmed by ^{1}H-NMR spectroscopy. The results are summarized in Table 1 along with the reaction conditions. The time-conversion plots of the reaction by vanadium catalysts are illustrated in Fig. 1.



(E)-Geraniol 2,3-Epoxygeraniol

Table 1. Catalytic epoxidation of (E)-geraniol.

Polymer resin	Metal	[Metal]/[Substrate]	Temp/°C	Time/h	%Conv.$^{a)}$	%Select.$^{b)}$
Gel-PMA	V	0.83×10^{-2}	80	4	100	98
	Mo	0.87×10^{-2}	80	24	89	81
MR-PMA	V	0.75×10^{-2}	80	1	100	98
	Mo	1.00×10^{-2}	80	24	94	78
	V	0.85×10^{-2}	20	8	92	96
Gel-HEA	V	0.94×10^{-2}	80	4	100	98
	Mo	0.90×10^{-2}	80	24	93	80
MR-HEA	V	1.00×10^{-2}	80	1.5	100	98
	Mo	1.10×10^{-2}	80	24	98	71
	V	1.03×10^{-2}	20	48	99	94
homogeneous	$VO(acac)_2$	1.40×10^{-2}	80	0.5	100	98

a) Conversion of (E)-geraniol. b) Percentage of 2,3-epoxygeraniol in the products; 6,7-epoxide, di-epoxide, and (E)-geranial were formed as minor products.

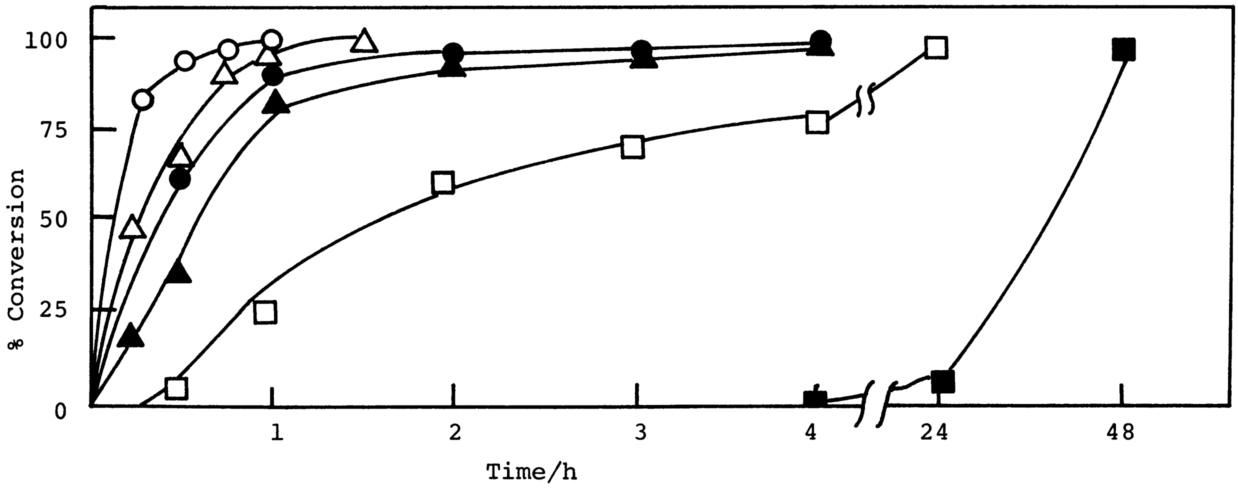


Fig. 1. Time-conversion of (E)-geraniol by polymer-anchored vanadium(V) complexes.
○ : MR-PMA resin at 80 °C, ● : Gel-PMA resin at 80 °C,
△ : MR-HEA resin at 80 °C, ▲ : Gel-HEA resin at 80 °C,
□ : MR-PMA resin at 20 °C, ■ : MR-HEA resin at 20 °C.

(E)-Geraniol was epoxidized preferentially at the olefinic site close to the hydroxyl group regardless of the metal ion, the functional group and the type of polymer matrix. Among the polymer catalysts examined here, the vanadium complex of MR-type resin was the most excellent one which showed a comparable reaction conversion, selectivity, and reaction rate to those of homogeneous $VO(acac)_2$ system. MR-type resin undergoes epoxidation at a much faster rate than the corresponding Gel-type resin (Fig. 1), presumably because the MR-type resin has large diameter pores10) which allow the facile diffusion of the substrate into the polymer matrix. It appeared that the catalytic activity of the vanadium complexes is generally higher than those by the molybdenum complexes. A similar trend has been observed in the homogeneous catalyst system.2) The epoxidation reaction proceeds under moderate temperature (20 °C) by use of the vanadium-MR-resin complexes. The vanadium complexes of MR-PMA and MR-HEA resins accomplished 92% (8 h) and 99% (48 h) conversion of (E)-geraniol, respectively. The time-conversion profile (Fig. 1) showed that the MR-HEA system requires rather long induction period.

As has been claimed earlier in the homogeneous catalyst system11) the high regioselectivity can be interpreted by the mechanism in which the coordination of the hydroxyl group of substrate and *t*-BuOOH to the metal ion at neighboring position is involved as a key intermediate. This may be supported by the fact that the rate of epoxidation by the present catalysts is retarded in the presence of large excess of *t*-BuOH which may compete with geraniol for the coordination to the metal ion.

Table 2. Recycling of the polymer-anchored vanadium(V) complexes in the epoxidation of (E)-geraniol.[a)]

Resin	% Yield of 2,3-epoxygeraniol at repeated run 1	2	3	4	5
MR-PMA	98	93	95	93	93
MR-HEA	98	94	93	93	93

a) Each run was carried out at 80 °C for 2 h.

The polymer-anchored vanadium complexes were recovered at the end of the first run and used repeatedly under identical conditions (Table 2). Approximately 2-3% of vanadium leaked out of the polymer beads in the first run, however the loss of the metal became less remarkable in the successive runs. It is noteworthy that the catalysts examined here revealed almost reproducible activity after five times recycling use.

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8) The Gel-type styrene-divinylbenzene copolymer was obtained from Kodak Chemical Co. and the MR-type resin was supplied by Mitsubishi Chemical Industry Co. Ltd.
9) The adsorbed metal ion was liberated from the resin by elution with 1 M NaOH. The metal ion in the eluate was analyzed with an atomic absorption spectrometer.
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