

# Sheet Polymer and its Complexes. II. Preparation and Catalytic Activity of Polymeric Tetrakisphenylporphyrin Films Crosslinked by 4,4'-Biphenylene-Bisulfoate

RONG-MIN WANG,<sup>1,2</sup> SHU-BEN LI,<sup>2</sup> YUN-PU WANG,<sup>1</sup> YU-FENG HE,<sup>1</sup> ZI-QIANG LEI<sup>1</sup>

<sup>1</sup> Department of Chemistry, Northwest Normal University, Lanzhou 730070, People's Republic of China, China

<sup>2</sup> OSSO Key State Laboratory, Lanzhou Institute of Chemical Physics, Academia Sinica, Lanzhou 730000, People's Republic of China

Received 17 June 1997; accepted 27 August 1997

**ABSTRACT:** The polymeric meso-tetra-(4,4'-biphenylene-bisulfo)-phenylporphyrin and its complexes (PMTBPBSOPP, M = Co, Mn, Cu, and Zn) have been prepared in the presence of phase-transfer catalyst and characterized with ultraviolet–visible spectra, infrared spectra, X-ray photoelectron spectroscopy, and scanning electron microscopy. Its catalytic activity in oxidation of cumene, ethylbenzene, and cyclohexene by molecular oxygen have been studied. Cumene afforded efficiently cumenol (1), acetophenone (2), together with a small amount of 4-methyl acetophenone (3). Ethylbenzene afforded efficiently  $\alpha$ -methylbenzyl alcohol (4) and acetophenone (5). Cyclohexene catalyzed by PCuTBPBSOPP in the presence of molecular oxygen afforded 1,2-cyclohexanediol (6) and 1,2-cyclohexanedione (7). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2027–2034, 1998

**Key words:** catalytic oxidation; metalloporphyrin; polymer; dioxygen

## INTRODUCTION

The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors like dioxygen, hydrogen peroxide, alkylhydroperoxide, sodium hypochlorite, or iodosobenzene into various organic molecules under mild conditions, remains a difficult challenge in the fields of chemical and biological catalysis.<sup>1</sup> The current progress of the research on synthetic metalloporphyrin catalysts has led to the development of several systems that are able to reproduce the heme-enzyme mediated oxygenation and oxidation reactions, at least in terms of reaction types, mechanisms, and, often, rates. However, in olefin epoxidations or

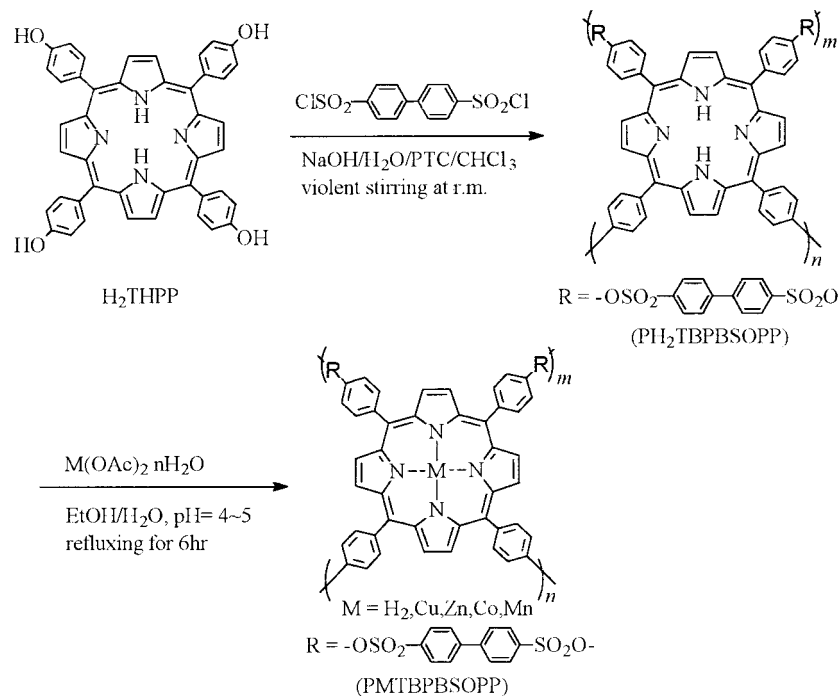
alkane hydroxylation, the oxygen source comes mainly from H<sub>2</sub>O<sub>2</sub>, alkylhydroperoxide, NaOCl, or PhIO. When dioxygen was used as oxidant, the reductant should be added into reactive system.

All the differential polymer porphyrins metal complexes used in catalyzed oxidation reaction can be classified in the following three categories. (1) metalloporphyrins were encapsulated into mineral supports, such as zeolite, silica, or clays; (2) metalloporphyrins were immobilized on the polymer (for instance, porous crosslinked polymer, linear polypeptides) by physical adsorption, covalent bond, ionic bond, or coordination bond; and (3) polymerization of metalloporphyrin derivatives. To our knowledge,<sup>2</sup> the reports about polymeric sheet porphyrin, which was used as a catalyst in oxidation, are very scarce.

In this article, polymeric sheet porphyrin, polymeric meso-tetra-(4,4'-biphenylene-bisulfo)-phe-

Correspondence to: R. M. Wang.

*Journal of Applied Polymer Science*, Vol. 67, 2027–2034 (1998)  
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/122027-08



Scheme 1

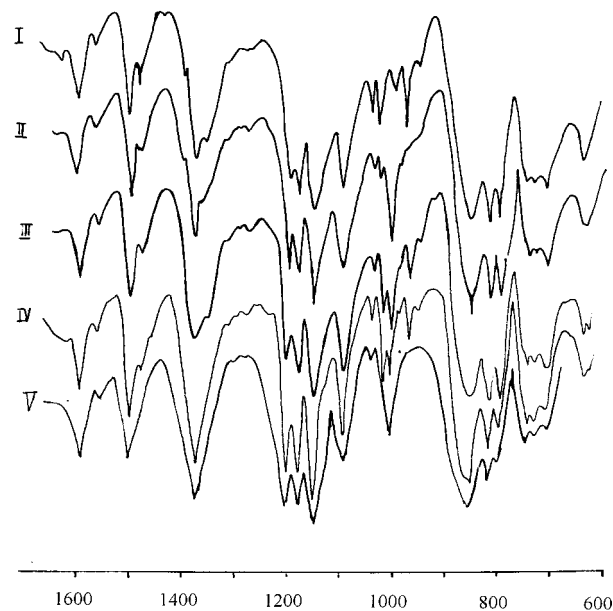
nylporphyrin and its complexes (PMTBPBSOPP) have been prepared; and its catalytic activity in oxidation of cumene, ethylbenzene, and cyclohexene by molecular oxygen have been studied. The synthetic route is as Scheme 1.

## EXPERIMENTAL SECTION

Pyrrole and propionic acid were freshly distilled before using. Chloroform was dried and distilled before using meso-tetra(*p*-hydroxyphenyl)porphyrin ( $\text{H}_2\text{THPP}$ ) was synthesized as per the method in the literature.<sup>2</sup> All other reagents used were of accepted grades of purity.

Small-area X-ray photoelectron spectroscopy (XPS) data were recorded with the PHI-5702 Multi-Technique System, power source by  $\text{MgK}_\alpha$  line, and  $\text{Ag } 3d_{5/2}$   $\text{FWHM} \leq 0.48$  eV. Ultraviolet-visible (UV-vis)-spectra were measured with a Hitachi U-3400 spectrophotometer. Infrared (IR) spectra were recorded in KBr disks with a Alphacentauri Fourier transform infrared (FTIR) spectrophotometer. Elemental analysis performed on Itali Carbo-Erba 1106 elemental autoanalyzer. The reaction products were determined and analyzed by using a Shimadzu QP-1000A gas chromatography-mass spectroscopy (GC-MS) system, a

GL-16A gas chromatograph with a  $5 \text{ m} \times 3 \text{ mm}$  OV-17 column, and GC-IR system a (HP 5890 II GC and Bio-Rad FTS 65A IR system; column,



**Figure 1** Infrared spectra of PMTBPBSOPP (in a potassium bromide tablet): (I)  $\text{PH}_2\text{TBPBSOPP}$ ; (II)  $\text{PCuTBPBSOPP}$ ; (III)  $\text{PCoTBPBSOPP}$ ; (IV)  $\text{PMnTBPBSOPP}$ ; and (V)  $\text{PZnTBPBSOPP}$ .

**Table I XPS Data of the Polymeric Porphyrin (PH<sub>2</sub>TBPBSOPP) and Its Complexes (PMTBPBSOPP)**

Compound	Binding Energy (eV)						
	C <sub>1s1/2</sub>	O <sub>1s1/2</sub>	S <sub>2p 1/2</sub>	N <sub>1s1/2</sub>		M <sub>2p 3/2</sub>	M <sub>2p 1/2</sub>
				N1 <sub>1s1/2</sub>	N2 <sub>1s1/2</sub>		
PH <sub>2</sub> TBPBSOPP	284.6	531.6	168.4	399.5	—	—	—
Co (OAc) <sub>2</sub>	—	—	—	—	—	Co	Co
PCoTBPBSOPP	284.6	531.7	168.6	399.6	398.1	779.6	795.0
M <sub>n</sub> (OAc) <sub>2</sub>	—	—	—	—	—	780.4	795.5
PMnTBPBSOPP	284.6	531.75	168.5	399.7	398.4	640.6	652.0
						M <sub>n</sub>	M <sub>n</sub>
						642.5	653.5

N<sub>1s1/2</sub> peaks of complexes were fitted by the fitting program.

SE54 (25 m × 0.32 mm); 60–240°C (10°C/min); inj., 280°C, Dect., 300°C).

H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH for several times. Yields of 80% or better of PMTBPBSOPP were obtained after drying.

#### The Polymeric Porphyrin Ligand: Meso-tetra-(4,4'-biphenylene-bisulfo)phenyl-porphyrin (PH<sub>2</sub>TBPBSOPP)

H<sub>2</sub>THPP (0.2 g) was dissolved in 10 mL solution of NaOH (1.25 mol/L) by stirring, and the phase transfer catalyst (30 mg) was added and then stirred for 20 min. To the solution, 5 mL of the solution of 4,4'-biphenylene disulfonyl chloride (0.25 g) were added dropwise in drying chloroform with vigorously stirring. The polymeric film was isolated by filtration and washed separately by water, EtOH, and chloroform three times. The product was obtained after drying (0.2 g; yield, 80%).

ANAL. Found (Calcd. for C<sub>68</sub>H<sub>42</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub>): C, 65.32 (66.13); H, 3.79 (3.40); N, 4.26 (4.54).

#### Preparation of PMTBPBSOPP

Coordination of polymeric ligand (PH<sub>2</sub>TBPBSOPP) with M(OAc)<sub>2</sub>·nH<sub>2</sub>O, (Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O) were performed in the mixture of H<sub>2</sub>O–C<sub>2</sub>H<sub>5</sub>OH (20 mL/20 mL). The molar ratio of PH<sub>2</sub>TBPBSOPP : M(OAc)<sub>2</sub>·nH<sub>2</sub>O is 1 : 10. The pH values were adjusted to 4–5 by dilute HOAc. The reaction mixtures were refluxed for 6 h with stirring. Products were filtered and washed separately by

#### The Oxidation Reaction

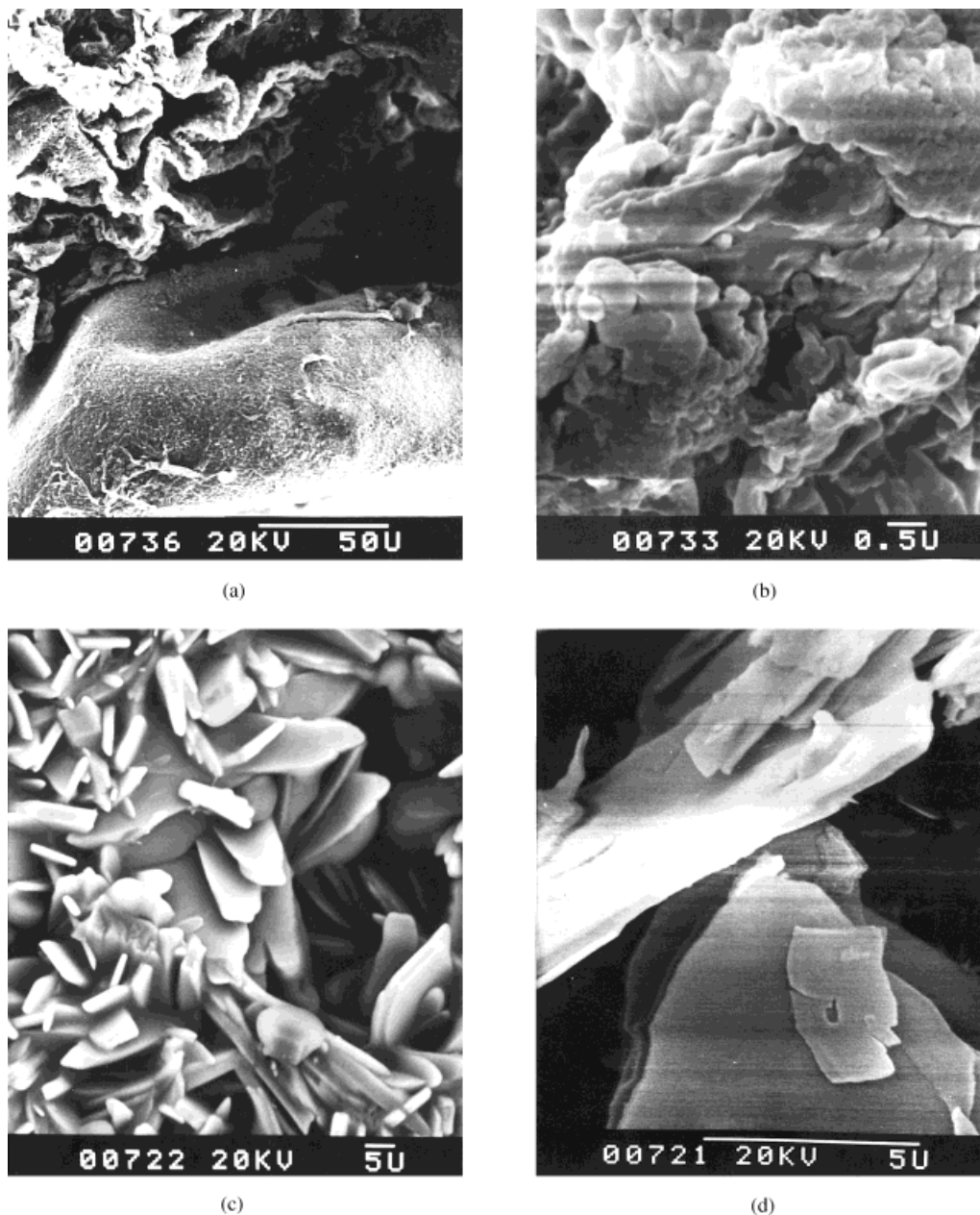
The oxidation of substrate was carried out in a glass reactor with a gas inlet tube connected to a gauge glass and a oxygen storage bottle with a gas outlet tube, which can be opened to the air if necessary. In a typical oxidation reaction, 15m mol of cumene and 6 mg of CoPTBPBSOPP were added in the 5 mL of the glass reactor. The oxygen was filled from the gauge glass, and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The reactor was put into heating bath, with a temperature of 70°C, and stirring was started. The consumption of oxygen was measured and calculated by gauge glass. After reacting for 9 h, the product was analyzed by GC, and the GC–MS and GC–IR systems.

## RESULTS AND DISCUSSION

### Characterization

#### Ultraviolet–Visible Spectra

The visible adsorption spectra of the PH<sub>2</sub>TBPBSOPP (M = H<sub>2</sub>, Co, Mn, Cu, and Zn) were recorded by KBr tablet. The polymeric ligand (PH<sub>2</sub>TBPBSOPP) exhibits a soret band at 422.1 nm, with the Q bands at 524.2, 558.7, 599.0, and 658.2 nm; it exhibits a



**Figure 2** Scanning electron micrographs of (a) the polymeric porphyrin  $\text{PH}_2\text{TBPBSOPP}$ , (b) the polymeric complex  $\text{PCoTBPBSOPP}$ , (c) the monomeric porphyrin  $\text{H}_2\text{TBSOPP}$ , and (d) its complex  $\text{CoTBSOPP}$ .

hyperchromic shift in copper or cobalt complex and a bathochromic shift in zinc or manganese complex. The number of polymeric ligand decreases from 5 to 2 because of the symmetry increase after coordination of metal.<sup>3</sup>

#### Infrared Spectra

Figure 1 shows the IR spectra of the polymeric ligand and its complexes (KBr). The absorption

of  $\text{S}=\text{O}$  double bond of symmetrical stretching vibration is near  $1178\text{ cm}^{-1}$ , and the asymmetrical stretching vibration is near  $1375\text{ cm}^{-1}$ . The weak absorption of  $\gamma_{\text{NH}}$  ( $3314\text{ cm}^{-1}$ ) and  $\delta_{\text{NH}}$  ( $966\text{ cm}^{-1}$ ) for the ligand disappear in zinc and copper complexes but only decrease in cobalt and manganese complexes. The strong absorption near  $1000\text{ cm}^{-1}$  appears to be a characteristic absorption for all metalloporphyrin,<sup>4</sup> and the absorption inten-

**Table II** Oxidation of Substituted Benzene Catalyzed by MPTBPBSOPP(M=Co, Mn, Cu)

Substrate	Catalyst (mg)	Temperature (°C)	Time (h)	Conversion (mol %)	Products Selectivity (mol %)
i-PrC <sub>6</sub> H <sub>5</sub>	CoPTBPBSOPP (6 mg)	70	9	23.7	97
i-PrC <sub>6</sub> H <sub>5</sub>	MnPTBPBSOPP (5 mg)	90	10	23.4	97
i-PrC <sub>6</sub> H <sub>5</sub>	CuPTBPBSOPP (5 mg)	85	10	10.0	96
i-PrC <sub>6</sub> H <sub>5</sub>	ZnPTBPBSOPP	—	—	—	—
Et-C <sub>6</sub> H <sub>5</sub>	CoPTBPBSOPP (9 mg)	70	8	13.8	99
Et-C <sub>6</sub> H <sub>5</sub>	MnPTBPBSOPP (5 mg)	60	9	6.5	98
Et-C <sub>6</sub> H <sub>5</sub>	CuPTBPBSOPP (5 mg)	90	9	trace	—
Et-C <sub>6</sub> H <sub>5</sub>	ZnPTBPBSOPP	—	—	—	—

Substrate: 15 mmol. The oxidation products were detected and analyzed by GC-16A gas chromatography (column; OV-17), QP-1000A GC-MS and GC-IR (HP 5890 II GC and Bio-Rad FTS 65A IR system. Column: SE54 (25 m × 0.32 mm); 60°C–240°C (10°C/min); Injector, 280°C; Detector 300°C).

sity of zinc or copper complex is stronger than that of cobalt or manganese complex. It showed that coordination of polymeric ligand with cobalt or manganese was not complete.

### X-ray Photoelectron Spectroscopy

In order to confirm the coordination of polymeric free-base porphyrin with manganese and cobalt. The small area XPS data of polymeric porphyrin and its complexes were measured (Table I).

Table I shows that the chemical shift of binding energy of carbon, oxygen, and sulfur is less than 0.2 eV. The chemical shifts of the metallic element are more than 0.5 eV. The nitrogen peak in complex could be divided into two peaks. Compared with ligand, the chemical shifts of N1<sub>1S1/2</sub> in complexes are less than 0.2 eV but N2<sub>1S1/2</sub> in complexes are more than 0.5 eV. This again indicates that coordination of polymeric ligand with cobalt or manganese are partly complete.

### Scanning Electron Microscopy

Figure 2 shows that the films of the polymeric porphyrin and its complexes have two-dimensional structures.

## CATALYTIC ACTIVITY

### Oxidation of Substituted Benzene

The results of the oxidation of substituted benzene by the MPTBPBSOPP (M = Co, Mn, and Cu)/O<sub>2</sub> system are listed in Table II. Cumene eff-

iciently afforded cumenol (1) and acetophenone (2), together with a small amount of 4-methyl acetophenone (3). According to the following equation,

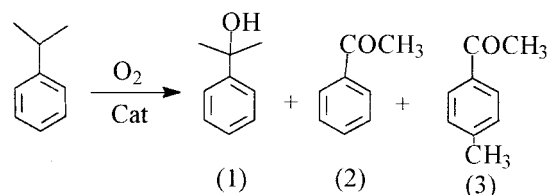
$$\frac{\text{Conversion of substrate (mol)}}{\text{Mole number of active center of catalyst}}$$

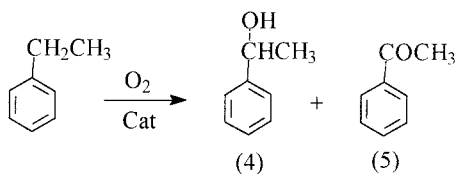
the turnover number was 742 for CoPTBPBSOPP after 9 h. Ethylbenzene efficiently afforded  $\alpha$ -methylbenzyl alcohol (4) and acetophenone (5). The oxidation is summarized in schemes 2 and 3. However, toluene could not be oxidized by O<sub>2</sub> in the presence of the polymeric porphyrins's complexes.

Figure 3 shows the relationship between the conversion of cumene and the reaction time (ML = PMBPBSOPP).

The conversions are influenced by reaction temperature. The activity of MPTBPBSOPP (M = Co, Mn, and Cu) were very low when temperature was controlled under 60°C, and it would be stable when the temperature was increased to near the boiling point (Fig. 4).

For comparing the activity of the monomeric complexes with the polymeric sheet metalloporph-

**Scheme 2**



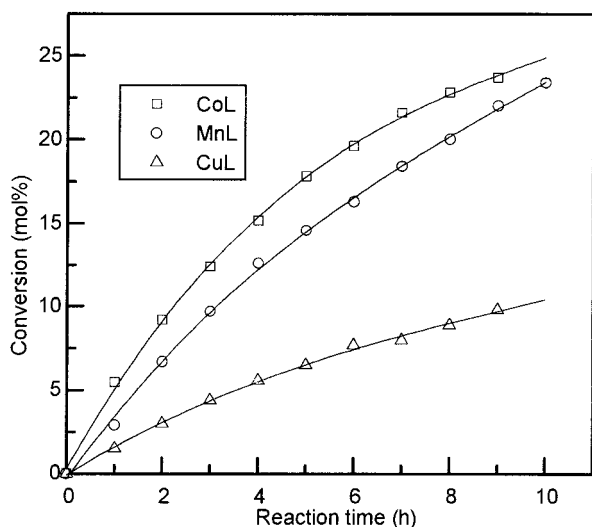
Scheme 3

yrin, the model compound [ $H_2TBSOPP$ , meso-tetra(4-benzenesulfonyl)phenyl porphyrin] and its complexes (MTBSOPP) have been synthesized and characterized. Figures 2(c) and (d) show their crystal shape. However, it was found that the consumption of oxygen was very small. It is considered that the molecular oxygen is easy to adsorb on the sheet surface of polymeric metalloporphyrin, but it is difficult to adsorb on the crystal surface or the solution of monomeric metalloporphyrin.

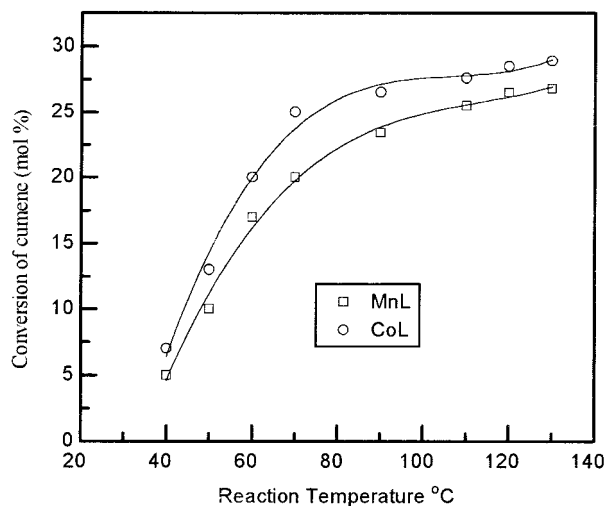
### Catalysis in Oxidation of Cyclohexene

In the field of metalloporphyrin-catalyzed olefin oxidation with molecular oxygen, the early approach was proposed by Tabushi, catalyzed by meso-tetrakisphenylporphyrinato manganese ( $MnTPPCl$ ) in the presence of sodium borohydride,<sup>5</sup> which afforded cyclohexanol and cyclohex-1-ene-3-ol. Groves and Quinn<sup>6</sup> reported that  $Ru^{VI}(-TMP)(O)_2$  catalyzes the aerobic epoxidation of olefins at room temperature and normal pressure.

In addition, Sharpless and coworkers found



**Figure 3** Relationship between conversion of cumene and reaction time [catalyzed by MPMBPBSOPP (mL)]. Conditions were the same as in Table II.



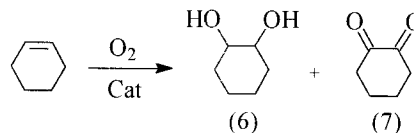
**Figure 4** Relationship between temperature and the catalytic activity of MPTBPSOPP.

that dihydroxylation of olefin is usually catalyzed by osmium or ruthenium complexes.<sup>7-9</sup> The configuration and enantiomeric excesses (% ee) of diols vary with ligands.

Here, it was found that oxidation of cyclohexene catalyzed by PCuTBPBSOPP in the presence of molecular oxygen afforded 1,2-cyclohexanediol (6) and 1,2-cyclohexanedione (7) without any solvent, and the selectivity to total ketone (7) and alcohol (6) is more than 77%. The results are listed in Table III.

The influence of base and acid to the catalytic activity and the product selectivity were investigated. When pyridine was added to the reaction mixture of cyclohexene and PCuTBPBSOPP as the catalyst, the conversion of cyclohexene increased from 13.2 to 22.5%, and the product selectivity of (6) and (7) increased from 77.9 to 81.3%; but the conversion was decreased by adding HOAc. Reaction rate was reduced dramatically by adding hexamethylene tetramine  $[(CH_2)_6N_4]$ . No activity of PZnTBPBSOPP or the monomeric copper-porphyrin complex (CuTHPP) was found in the oxidation of cyclohexene under the same condition (Scheme 4).

In living organisms, the introduction of an oxy-



Scheme 4



8. G. A. Crispino, P. Y. Ho, and K. B. Sharpless, *Science*, **259**, 64 (1993).
9. K. B. Sharpless, W. Amberg, M. Beller, H. Chen, Y. Kawanami, D. Lubben, E. Manoury, Y. Ogino, T. Shibata, and T. Ukita, *J. Org. Chem.*, **56**, 4585 (1991).
10. P. R. Ortiz de Montellano, *Cytochrome P-450 Structure, Mechanism and Biochemistry*, Plenum Press, New York, 1990.
11. D. Mansuy, *Pure Appl. Chem.*, **62**, 741 (1990).
12. M. Shimizu, H. Orita, T. Hayakawa, and K. Takehira, *J. Mol. Catal.*, **53**, 165 (1989).
13. J. Haber, T. Mlodnicka, and M. Witko, *J. Mol. Catal.*, **52**, 85 (1989).
14. J. E. Lyons, P. E. Ellis, and V. A. Durante, *Stud. Surf. Sci. Catal.*, **67**, 99 (1991).
15. P. E. Ellis and J. E. Lyons, *Catal. Lett.*, **8**, 45 (1991).