Table 1. Catalytic Activities of Ni(II)-Macrocyclic Complexes for Oxidation of Styrene

$(N_{uc}/N_t)^a$	Styrene oxide	Benzaldehyde	Phenylacet-aldehyde
$\mathbf{A}_1^b$ (0/4)	94^d $(18.8)^e$	5 (1.2)	1 (0.2)
$\mathbf{A}_2^c$ (0/4)	94 (18.2)	7 (1.4)	2 (0.4)
B (1/5)	78 (15.6)	6 (1.3)	15 (3.1)
C (2/6)	77 (15.4)	14 (2.8)	9 (1.8)
D (2/6)	71 (14.2)	9 (1.8)	18 (3.6)
E (2/6)	67 (13.4)	5 (1.2)	25 (5.1)
F (2/6)	67 (13.4)	8 (1.6)	25 (5.1)
G (2/8)	63 (12.6)	7 (1.4)	23 (4.7)

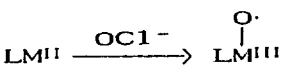
Experimental conditions were complex (0.05 mmol), styrene (1 mmol), NaOCl (4 mmol), acetonitrile (5 m*l*), temp. (40℃), and time (5 hr). $^a N_{uc}$ = un-coordinated nitrogen number on complex, N_t = total ni-trogen number in ligand. ^{b}meso-, ^{c}racemic-, ^{d}Yields (%) were based on initial styrene concentrations. ^{e}turnover.

Table 2. Catalytic Activities of Cu(II)-Macrocyclic Complexes for Oxidation of Styrene

$(N_{uc}/N_t)^a$	Styrene oxide	Benzaldehyde	Phenylacet-aldehyde
F (2/6)	53 (10.6)	27 (5.4)	20 (4.0)
B (1/5)	51 (10.2)	27 (5.4)	22 (4.3)

All experimental conditions and explanations were the same as in Ni(II)-system.

hyde (yields based on styrene and turnovers based on complex). However, when ligands with uncoordinating nitrogen atoms were used (**B**-**G**) yield of styrene oxide decreased and that of phenylacetaldehyde increased. For example, Ni(**G**)$^{2+}$ (octaazamacrocyclic complex) gave 63% of styrene oxide and 23% of phenylacetaldehyde. Role of the uncoordinating nitrogen atoms in the catalytic reaction is currently under investigation. Meso-Ni(**A**)$^{2+}$ and racemic-Ni(**A**)$^{2+}$ isomers showed almost the same product distribution which indicates that catalytic activity is not affected by the small steric effect due to the different methyl group arrangements of meso- and racemic-A. Small amounts (5-9%) of benzaldehyde as C=C cleavage product[4] were observed in all nickel(II) complex systems except for Ni(**C**)$^{2+}$ (non-cyclic hexaazaligand) (14 %). Cu(**F**)$^{2+}$ and Cu(**B**)$^{2+}$ were observed less effective catalysts for the formation of styrene oxide. However, yields of benzaldehyde were increased in copper(II) complexes more than nickel(II) complexes. Hydrogen peroxide and *tert*-butyl hydroperoxide were ineffective as an oxidant for styrene epoxidation.



$$\mathrm{LM^{II}} \xrightarrow{\mathrm{OCl^-}} \overset{\mathrm{O\cdot}}{\overset{|}{\mathrm{LM^{III}}}}$$

1

The mechanism of the present catalytic oxidation of styrene has not new elucidated. Several mechanisms have been proposed in the similar systems[3-5]. However, the structure of the active species generated from the reaction of nickel(II) and copper(II) polyazamacrocyclic complexes with NaOCl was still unknown. Recently, structure **1** was reported a likely candidate for the active species formed with complex and OCl$^-$. We believe that the same species might also be invaluable in our systems. **1** has considerable radical character at the oxygen, its addition to an styrene would proceed in stepwise to generate products observed.

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Cyclopolymerization of 4-Hydroxy-4-phenyl-1,6-heptadiyne Containing Hydroxy Functional Group by Transition Metal Catalysts

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There have been many studies on polyacetylene[1] because of its unique properties. Polyacetylene is, however, unstable in air and insoluble in ususal organic solvents. Thus, though the electrical conductivity is somewhat low, studies of the synthesis and properties of substituted polyacetylene which

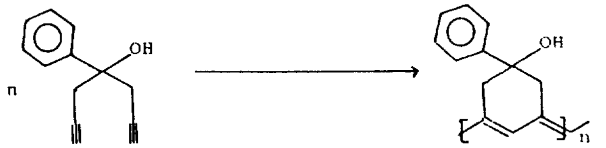
Table 1. Polymerization of 4-Hydroxy-4-phenyl-1,6-heptadiyne by Various Catalyst System[a]

Exp. No.	Catalyst System (:) mole ratio[b]	Polymer Yield (%)
1	$MoCl_5$	98
2	$MoCl_5$ $(n\text{-}Bu)_4Sn$ (1 : 2)	85
3	$MoCl_5$ $EtAlCl_2$ (1 : 2)	76
4	WCl_6	0
5	WCl_6 $(n\text{-}Bu)_4Sn$ (1 : 2)	0
6	WCl_6 $EtAlCl_2$ (1 : 2)	5

[a] Polymerization was carried out in dioxane at 60℃ for 24 hrs. Initial monomer concentration $[M_o]$ was 1.0 M and monomer to catalyst mole ratio was 50. [b] Mixture of catalyst and cocatalyst was aged at 30℃ for 15 min before use.

are soluble and relatively stable in air has been intensively investigated.[2] Since various substituted acetylenes have been polymerized to conjugated polymers by transition metal catalysts, the cyclopolymerizations of nonconjugated diynes were investigated in an attempt to prepare a polymer that would containing alternating double bond and single bonds along the polymer backbone and a cyclic recurring unit.[3] We reported that 1,6-heptadiyne derivatives were cyclopolymerized by transition metal catalysts.[4-7] However, it has been known that the acetylenic monomers containing hydroxy functional group were hardly polymerized by transition metal catalysts. Recently, we found that Mo-based catalysts polymerized dipropargylcarbinol(4-hydroxy-1,6-heptadiyn) containing hydroxy functional group.[8] However, the molecular weight of poly(4-hydroxy-1,6-heptadiyne) was barely several thousand and the properties had depreciated.

The present communication reports the study on the cyclopolymerization of 4-hydroxy-4-phenyl-1,6-heptadiyne (HPH) containing hydroxy group and phenyl substituent at 4-position.



All the procedures of the preparation of catalysts, and polymerization were carried out under dry nitrogen atmosphere.[5]

Table 1 shows the results of the polymerization of 4-hydroxy-4-phenyl-1,6-heptadiyne by various catalysts. The $MoCl_5$-based catalysts have all effective catalytic activity. However, poly(HPH) is hardly obtained by using WCl_6-based catalysts. It seems that functional hydroxy group in monomer inhibits catalytic activity of WCl_6, though hydroxy group is considerably hindered by bulky phenyl substituent. $(n\text{-}Bu)_4Sn$ and $EtAlCl_2$ have been known to be an excellent cocatalyst for the polymerization of mono- and di- substituted acetylenes.[9,10] However, neither $(n\text{-}Bu)_4Sn$ nor $EtAlCl_2$ have any effect as a cocatalyst of $MoCl_5$ and WCl_6 on the cyclopolymerization of HPH. HPH is effectively polymerized by $MoCl_5$ alone.

The obtained highly colored (red black) poly(HPH) is completely soluble in common organic solvents. The ^{13}C-NMR spectrum of poly(HPH) shows the chemical shifts at 130 and 140 ppm due to the polyconjugated olefinic carbon. The IR spectrum also shows the conjugated carbon-carbon double bond stretching at 1600-1650 cm^{-1}. In the UV-visible spectrum of poly (HPH), a characteristic peak of conjugated polymers, broad $\pi-\pi^*$ absorption, appears at visible region (300-700 nm) with maximum 500 nm.

In the above spectroscopy data and solubility behavior, we suggest that poly(HPH) possesses polyene structure having cyclic recurring units in the polymer backbone.

The number average molecular weights ($\overline{Mn}$) of poly (HPH) are in the range of 20000-30000, although that of poly(4-hydroxy-1,6-heptadiyne) only reaches several thousand.

More detailed studies on the cyclopolymerization of 1,6-heptadiyne derivatives containing hydroxy group and various substituents by transition metal catalysts and the physcial properties of resulting polymers are in progress.

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Preparation and Reaction of Carbohydrate Cyclic Sulfates: Efficient Synthesis of O^2,2'-Cyclopyrimidine Nucleoside and Ara-U

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Cyclopyrimidine nucleosides have been served as valuable models for physicochemical studies on the base-sugar con-