

CHAPTER 1

INTRODUCTION

1.1 Salens and their applications

Tetradentate Schiff base containing N and O atom donors, N,N'-bis(salicylaldehyde)ethylenediamine or salen, is a well-known class of ligands for complexing transition metal ions. Because of its ease of synthesis, its high complexation ability with various metal ions and its planar structure, salen has attracted much attention.

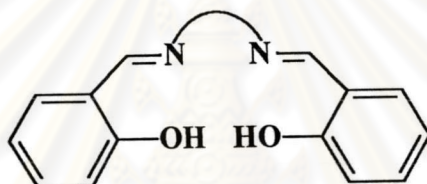


Figure 1.1 The general structure of salen.

It has been found that metal-salen complexes can show many interesting properties such as DNA cleaving¹, sensing²⁻⁴ and asymmetric catalysis⁵⁻⁹. Not only the small molecular salens but also polymeric salens have been extensively studied. Polymeric salens show some interesting properties different from small molecular salens. The development of salens and their applications are described in the following sections.

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1.1.1 Liquid Crystal

Salens illustrated in Figure 1.2 manifested an enantiotropic smectic C phase¹⁰. Liquid crystal property of these ligands is a result of an intramolecular H-bonding between hydrogen of the hydroxyl group and the iminic nitrogen, forming six-membered ring. Consequently, the planarity and polarizability of the molecules were increased as the rotation of several bonds become more restricted.

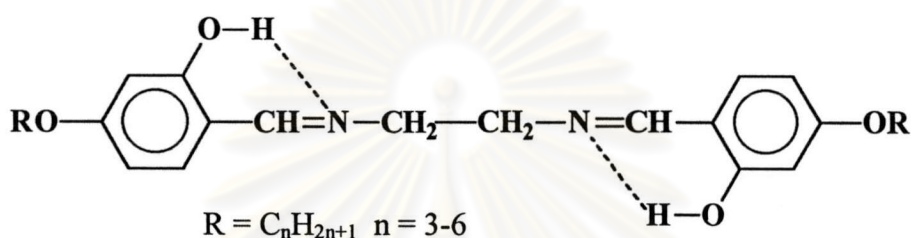


Figure 1.2 The structure of salens with liquid crystal property.

The effect of the chain length of the alkyl substituents of these salens were also studied and found that short terminal chains exhibited nematic mesophase while the longest chain showed smectic mesophase. The intermediate chain length displayed both nematic and smectic mesophase. The strong dipole-dipole interaction, together with the length of the molecules, made misalignment of the molecules more difficult resulting in a formation of smectic phase.

The incorporation of copper into Schiff base (L) ligand (Figure 1.3) led to a more ordered mesophase¹¹. Geometrically, CuL_2 was more symmetric than L as the copper ion increased the planarity of the ligands.

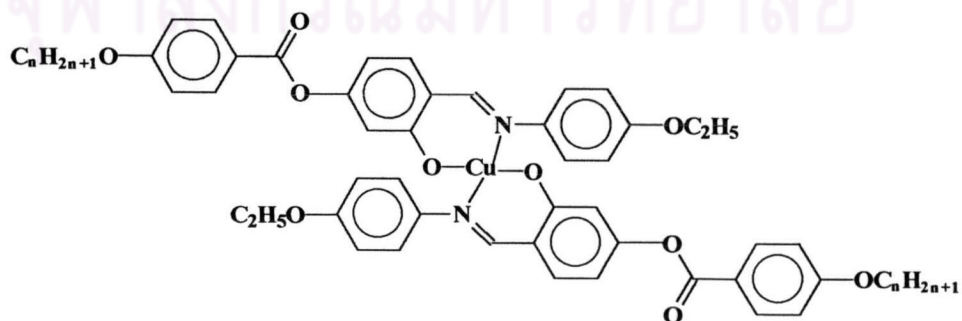


Figure 1.3 The structure of copper salen complex.

1.1.2 Electrochemical sensors

1.1.2.1 Nitric oxide

The electropolymerized film of Ni-salen (Figure 1.5) on a Pt electrode could be used as an electrochemical sensor for determination of nitric oxide. This sensor displayed very low detection limit (5×10^{-9} mol/L), high sensitivity and selectivity to NO and is promising for *in vivo* measurements of NO².

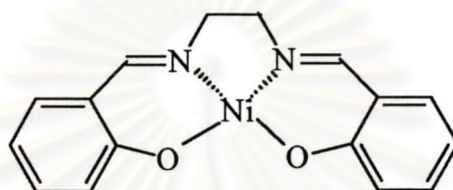


Figure 1.5 The structure of Ni-salen electropolymerized for NO sensing.

Additionally, cobalt, copper, iron and manganese were also used as central ions for the complexes. The similar activity toward NO oxidation of the sensors based on polymeric M(salen) with different central ions were obtained with only little difference of the detection limit³.

1.1.2.2 Imino compounds

The electropolymerized film of copper complex of the half-unit 2,6-diacetylpyridine-mono(ethylenediamine) (Figure 1.6) on glassy carbon could carry out indirect electrochemical reduction of imino agrochemical compounds (Figure 1.7), which affect to the biological tissues⁴. Cyclic voltammetry confirmed that this modified electrode was able to reduce the imino moiety to the corresponding amino group at a lower potential than that of the classical glassy carbon electrode.

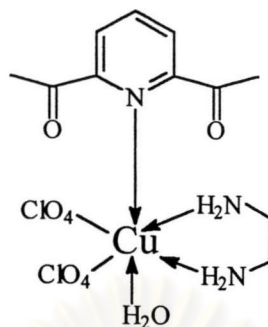
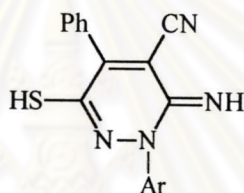


Figure 1.6 The structure of copper complex electropolymerized for testing electroreduction of imino compounds.



Ar = C₆H₅, C₆H₄-CH₃, C₆H₄-NO₂, C₆H₄-Cl

Figure 1.7 Series of imino compounds used in electroreduction study.

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1.1.3 Asymmetric catalysts

Metal salen complexes are one of the most rapidly established class of asymmetric catalysts. With the growth in interest in enantiomerically pure compounds for the pharmaceutical and agrochemical industries, it is not surprising that in the last decade attention has focused on chiral salen ligands, and in particular on the use of their optically pure metal complexes as asymmetric catalysts. By changing the central metal ions, metal complexes of salens can catalyze various reactions with a good yield and high enantiomeric excess.

The chiral Mn(III)-schiff base complex⁵, known as Jacobsen's catalyst, is currently one of the most efficient catalyst available for the enantioselective epoxidation of unfunctionalised olefins (Figure 1.8). Enantioselective epoxidations of simple olefins using only 2-5 mole percent of Jacobsen's catalyst gave epoxide up to 97% yield with an asymmetric induction as high as 98% enantiomeric excess depending on the substrates.

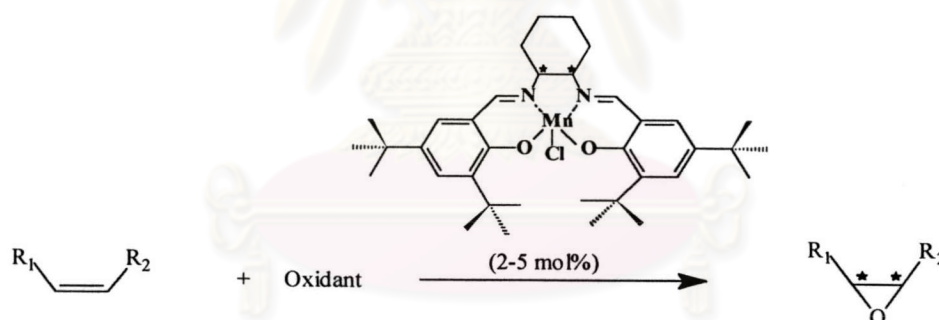


Figure 1.8 Use of Mn-salen complex in epoxidation of unfunctionalised olefin.

Additionally, cobalt⁶ and titanium⁷ salen complexes were also effective catalysts for hydrolytic kinetic resolution of epoxide and trimethylsilylcyanation of benzaldehyde, respectively, with both good yield and excellent enantiomeric excess.

The catalytic properties of small molecular salen complexes were already widely studied, therefore the study of polymeric salens were the latest outstanding topic for the researchers.

The copolymerization of styrene and divinylbenzene with Jacobsen's catalyst yielded the corresponding crosslinked polymers (Figure 1.9)⁸.

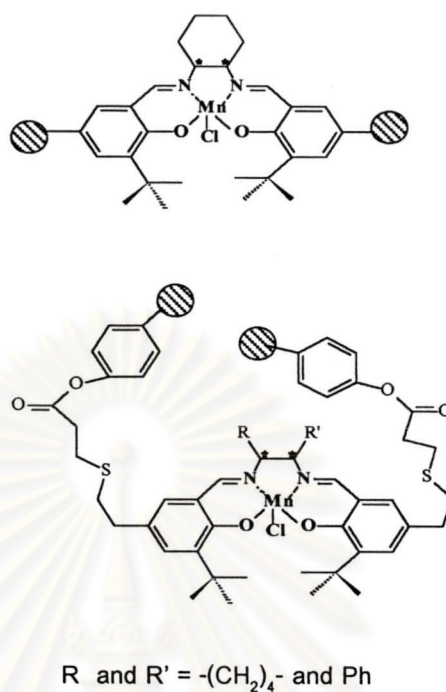


Figure 1.9 Jacobsen's catalyst linked with polymer in heterogeneous system.

Although these insoluble catalysts epoxidised unfunctionalised alkenes with good yields, the enantioselectivity was rather disappointing (1-62 %ee). The poorer enantiomeric purity obtained relative to that found with the homogeneous system may be the result of the rigidity of the catalyst structure. While the small molecular salen complexes showed high activities and enantioselectivities, the polymeric salens provided potential for recovery and recyclizibility. The activities and enationselectivities remain challenging in the development of novel heterogeneous catalytic systems.

Polymeric Mn-salen complexes with the flexible linker between each salen unit were synthesized (Figure 1.10)⁹. The enantiomeric excess of products obtained from these catalysts were improved (25-91 %ee) almost as high as homogeneous system. The flexible chain increase the solubility of the catalysts in the reaction medium. Moreover, the catalysts could be precipitated in an appropriate solvent and recycled effectively several times resemble to heterogeneous catalysts.

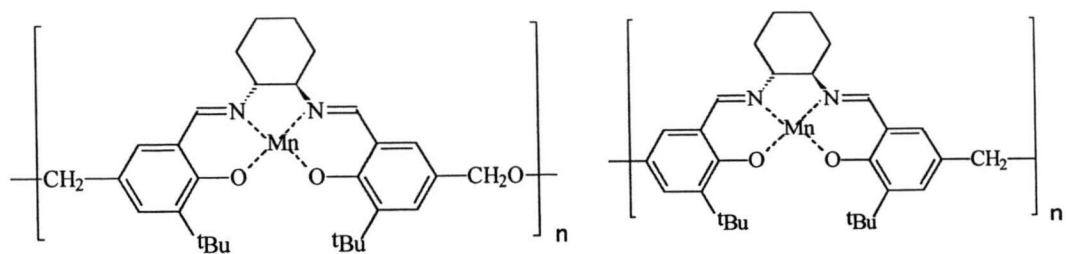


Figure 1.10 polymeric Mn-salen with flexible linkers.

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1.2 Gel permeation chromatography^{13,14}

Although not a primary method for determining molecular weights, gel permeation chromatography (GPC) or size exclusion chromatography (SEC) has developed into one of the most useful methods for routine determination of average molecular weights and molecular weight distributions of polymers.

GPC is a form of liquid chromatography in which the molecules are separated according to their molecular size. The procedure involves injecting a dilute solution of a polydisperse polymer into a continuous flow of solvent passing through a column containing tightly packed microporous gel particles. The gel has particle sizes in the range 5-10 μm in order to give efficient packing and typically possesses a range of pore sizes from 0.5 to 10^5 nm, which correspond to the effective size range of polymer molecules. Separation of the molecules occurs by preferential penetration of the different sized molecules into the pores; small molecules are able to permeate more easily through the pores compared to the larger sized molecules so that their rate of passage through the column is correspondingly slower. The continuous flow of solvent leads to separation of the molecules according to size with the larger molecules being eluted first and the smaller molecules, which have penetrated more deeply into the pores, requiring longer elution times. It follows that the time or, more usually volume of the elution, is inversely proportional to the molecular size. If the pore size is too small to permit penetration by any of the molecules, or if the pore size is so large that all of the molecules can penetrate with the same relative ease, there would be little or no separation of the molecules. Consequently, selection of the column packing material to have the appropriate pore size distribution is crucial and different columns are usually required for polymers having widely different molecular weight distributions.

The essential requirements for a GPC chromatograph (Figure 1.11) are:

1. Solvent delivery system: capable of maintaining a constant linear velocity flow.
2. Column(s) containing suitable microporous gel particles to produce the necessary size separation.
3. Injection system: capable of delivering accurately small volumes of sample solutions without disturbing the solvent flow.

4. Detection system to monitor output from the columns and to provide continuous quantitative and possibly qualitative data on the fractions being eluted.
5. Recorder to give continuous output traces.

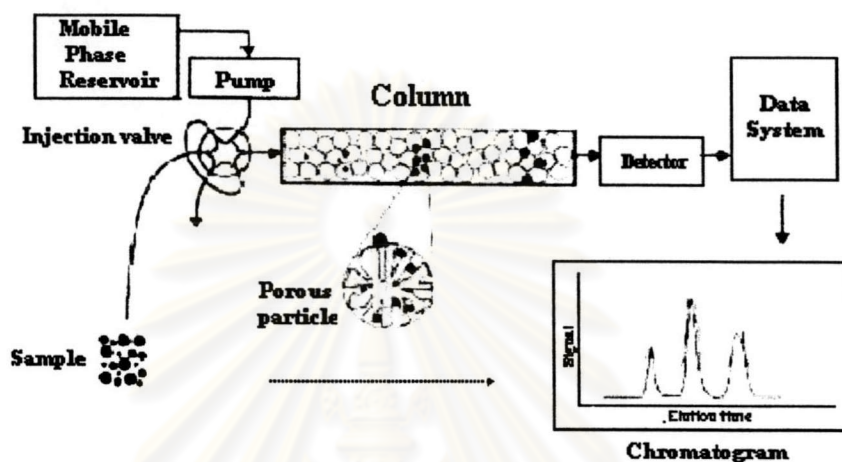


Figure 1.11 Schematic of typical gel permeation chromatograph.

A typical gel permeation chromatogram (Figure 1.12) plots detector response against the volume of dilute polymer solution that passes through the column (the elution volume, V_r). To obtain molecular weights at a given retention volume, the chromatogram may be compared with a reference chromatogram obtained with fractions of known average molecular weight in the same solvent and at the same temperature.

The major problem with calibrating a particular GPC column for a particular polymer is that few standard samples of narrow molecular weight distribution are available commercially. Polystyrene standards having polydispersity indexes close to unity are available over a wide range of molecular weights (600–2.5 million) and these are often used: if one is dealing with a polymer other than polystyrene, however, the molecular weights thus obtained are at best approximate and may in some instances be seriously in error. To circumvent this difficulty, the universal calibration method is employed.

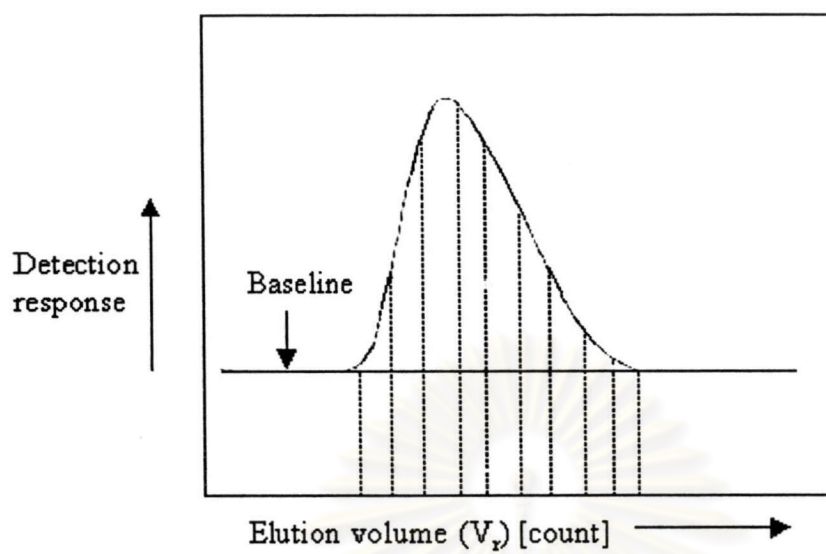


Figure 1.12 The typical gel permeation chromatogram

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1.3 Cyclic Voltammetry¹⁵

Nowadays, sensor based on electrochemical techniques has become an important tool for detection of numerous substances due to the electrochemical sensor possesses comparatively low detection limit, high selectivity and sensitivity, and quick response to analytes. Among many methods in electrochemical measurement, cyclic voltammetry is the most popular techniques for the study of mechanisms and rates of oxidation/reduction processes, particularly in organic and inorganic systems.

Cyclic voltammetry is based on the same principles as linear sweep voltammetry. In this technique, as shown in Figure 1.13, the initial potential (E_i) of the working electrode is increased linearly with the time until reaching a certain value (E_s), so-called switching potential, the potential is then scanned back.

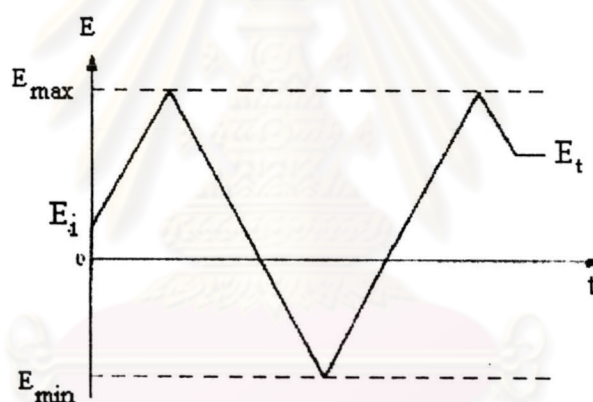


Figure 1.13 Cyclic voltammetric excitation signal used to obtain voltammogram.

In Figure 1.13, the reverse scan is set to the end at the initial potential, but this does not have to be the case in every cyclic voltammetric experiment.

The key advantage of cyclic voltammetry over linear scan voltammetry results from the reverse scan. Reversing the scan after the electrochemical generation of species is a direct and straightforward way to probe its stability. A stable electrogenerated species will remain in the vicinity of the electrode surface and yield a current wave of opposite polarity to that observed in the forward scan. An unstable species will react as it is formed and no current wave will be detected in the reverse scan.

The curve which show the relationship between current and voltage is called cyclic voltammogram. A typical cyclic voltammogram is shown in Figure 1.14.

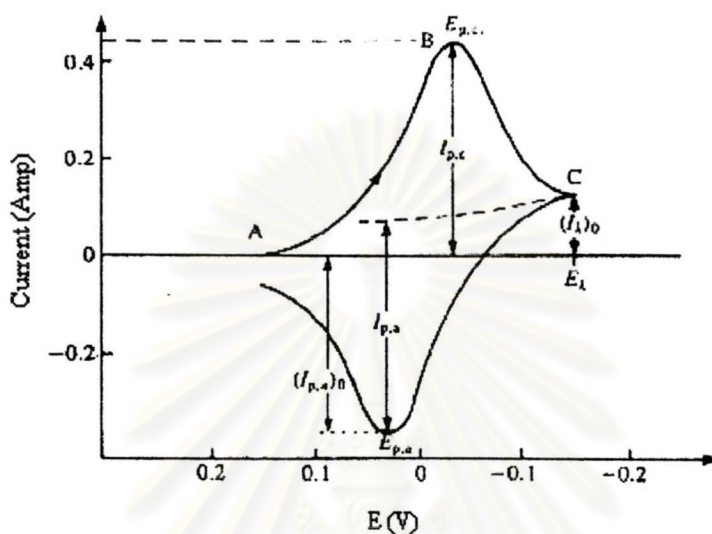


Figure 1.14 Cyclic voltammogram.

There is a peak formed in both the forward and reverse sides of the cyclic voltammogram. Oxidation has occurred during forward part of the scan, with reduction taking place during the reverse part. If the scan was going negative from E_i , then reduction would occur during the forward part of the scan, and oxidation during the reverse. Normally, cyclic voltammogram could be used as an important tool to define the reversibility of a redox reaction. The reversibility of a redox couple could be decided from cyclic voltammogram only if.

1. $I_{pc} = I_{pa}$
2. The peak potentials, E_{pc} and E_{pa} , are independent of the scan rate (v).
3. E^0 is positioned midway between E_{pc} and E_{pa} , so

$$E^0 = (E_{pa} + E_{pc})/2$$

4. I_p is proportional to $v^{1/2}$

5. The separation between E_{pc} and E_{pa} is $59/n$ mV for an n electron transfer type.

*pc = peak cathodic, pa = peak anodic

The redox couple is almost certainly not reversible if one or more of these criteria are not fulfilled.



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1.4 Objectives and scope of the research

Salen compounds possess numerous interesting properties such as liquid crystal property, nitric oxide sensing and asymmetric catalysis. Polymeric salens probably have the different interesting properties from small molecular salens because of their polymer characters. However, polymeric salens, nowadays, encounter a problem in solubility due to the rigidity of the salen building block. This problem limited many benefits of salen polymers as well as their complexes.

To increase the solubility of these compounds, in this project, the flexible glycolic chains were incorporated into the salen ligand. Moreover, the glycolic chain length were varied to investigate the effect of flexible chain to the solubility of salen polymers and their complexes.

Furthermore, our interest is also concentrated on the use of polymeric salen complexes as an electrochemical sensor. Many analytes were also examined to find out the selectivity of these modified polymeric salen sensors.



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