

Synthesis and Characterization of Poly(Selenium Coronands)

by

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## ABSTRACT

Polymers with pendant selenium coronands, 1, 5-diselenacyclooctane (8Se<sub>2</sub>) and 1, 5, 9, 13-tetraselenacyclohexadecane (16Se<sub>4</sub>) have been prepared by free radical polymerization of selenium coronands derivatized with acryloyl groups. Copolymers were also prepared by copolymerization of methyl acrylate with 3, 7-diselenacyclooctyl acrylate. These polymers and copolymers were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and UV-visible spectroscopy, mass spectrometry, atomic absorption spectroscopy, gel permeation chromatography, differential scanning calorimetry and cyclic voltammetry.

UV-visible spectroscopy has been used to monitor interactions between the polymers and different metal ions. Significant interactions were observed with eleven metal ions for the polymer containing 8Se<sub>2</sub>, whereas polymers containing 16Se<sub>4</sub> showed interactions only with Cu<sup>2+</sup>, Te<sup>4+</sup>, Fe<sup>3+</sup>, and Pd<sup>2+</sup>. These interactions are attributed to complexation. The polymer-Cu complexes have been characterized by atomic absorption spectroscopy.

Polymers with pendant selenium coronands exhibit a rich redox chemistry, much like the monomeric selenium coronands. These polymers can be oxidized both chemically (NOBF<sub>4</sub>) and electrochemically. Cyclic voltammetric studies suggest the presence of inter- and intra-selenium coronand electron transfer processes. Relative to monomeric selenium coronands, irreversible reactions between oxidized species and neutral ligands are suppressed by tethering the coronands to polymer chains. This behavior is observed for the polymers in solution and coated on electrodes

(polymer modified electrodes). The phenomenon represents partial control of the fate of reactive species by steric constraint.

Polymer-coated electrodes were tested for their ion-selective properties. A linear relationship of potential versus concentration was obtained for  $\text{Cu}^{2+}$  ion.

## DEDICATION

To my parents

To my wife

To my son

## ACKNOWLEDGEMENTS

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## LIST OF SYMBOLS AND ABBREVIATIONS

AAS	atomic absorption spectroscopy
AIBN	2,2'-azobis(isobutyronitrile)
CE	counter-electrode
Cop8Se2-A	copolymer with the ratio of 8Se2 to OCH <sub>3</sub> of 1.4 : 1
Cop8Se2-B	copolymer with the ratio of 8Se2 to OCH <sub>3</sub> of 0.75 : 1
CV	cyclic voltammetry
DSC	differential scanning calorimetry
EC	electrochemical-chemical process
GPC	gel permeation chromatography
ISEs	ion selective electrodes
Mono16Se4	1,5,9,13-tetraselenacyclohexadecyl acrylate
Mono8Se2	1,5-diselenacyclooctyl acrylate
Poly8Se2	poly(1,5-diselenacyclooctyl acrylate)
Poly16Se4	poly(1,5,9,13-tetraselenacyclohexadecyl acrylate)
RE	reference electrode
RI	refractive index
16Se4	1,5,9,13-tetraselenacyclohexadecane
16Se4-OH	3-hydroxy-1,5,9,13-tetraselenacyclohexadecane
8Se2	1,5-diselenacyclooctane
8Se2-OH	3-hydroxy-1,5-diselenacyclooctane
SEC	size exclusion chromatography
TEAP	tetraethylammonium perchlorate
THF	Tetrahydrofuran
WE	working electrode or studying electrode
Γ	Surface coverage (mol/cm <sup>2</sup> )



# Chapter 1

## INTRODUCTION

### 1.1. Background

Studies in multidentate macrocyclic compounds (or crown compounds) have continually increased since Pedersen first reported the synthesis of crown ethers in 1967<sup>[1a]</sup>.

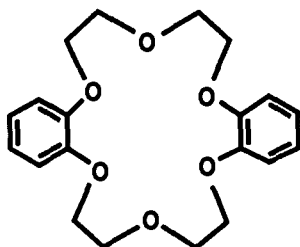


Figure 1. Structure of dibenzo-18-crown-6

In 1962, Dr. C. J. Pedersen identified a macrocyclic polyether (e.g. dibenzo-18-crown-6, see Figure 1.) as an unexpected by-product and discovered that it had the unusual property of complexing with alkali anions<sup>[1b]</sup>. He subsequently synthesized a series of macrocyclic polyethers, which he named "crown compounds"<sup>[1a]</sup>. After that, the chemistry and applications of crown compounds have been elaborated rapidly, and with remarkable results. Several hundred novel crown compounds and their

analogues, including aza- and thiacrown compounds, cryptands, optically active crown compounds have been synthesized and their specific properties investigated<sup>[2]</sup>. The more recent additions to this list include selenium crowns<sup>[3]</sup> and polymeric crown compounds<sup>[2]</sup>. In addition to basic research, research into the applications of crown compounds has been fruitful in a wide variety of fields such as organic synthesis, polymer synthesis, analytical chemistry, capture and separation of metal ions, resolution of optical isomers, biochemistry and biophysics. Several types of crown compounds have been put to practical use<sup>[1b]</sup>.

It is the unique properties of crown compounds that promises to break fresh ground in such new areas of science as "host-guest chemistry" and "biomimetic chemistry", which are at the interface between chemistry and biology. Crown compounds may also lead to innovative technologies. This potential is surely the principal explanation for the great attention paid to crown compounds and for the rapid progress in research on their chemistry and applications.

### **1.1.1. Definitions of Crown Compounds**

Crown compounds were so named because of their chemical structure and the shape of the complex formed when metal ions were enclosed in the cavity. Crown compounds have not yet been strictly defined, but they are generally described as "macrocyclic compounds having hetero atoms such as O, N, S, and Se in their ring structure and the property of incorporating cations into their cavities".

There are many different names for crown compounds, such as macrocyclic polyether, cyclic polyether, crown ether, thiacycrown ether or crown thiaether, cyclic polythiaether, selenacycrown ether, macrocycle, azacycrown or azacycrown ether, coronand, cryptand or multicyclic crown, cyclam, podand, etc.. Vogtle and Weber [2] have proposed the use of the terms coronand, crown ether, crown thiaether, cryptand cyclam, and podand according to the following definitions.

**Coronand:** Any medium sized or macrocyclic system having only one ring and containing any heteroatom(s).

**Cryptand:** Bi- and polycyclic compounds containing any heteroatoms.

**Cyclam:** The all-nitrogen heteromacrocycles.

**Podand:** Open-chain (acyclic) analogs of either coronands or cryptands.

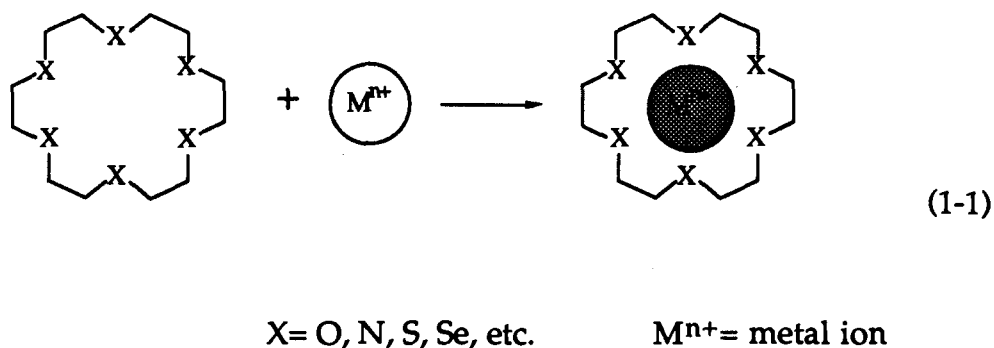
**Crown ether:** This term would refer specifically to coronands containing only oxygen heteroatoms in the ring.

**Crown thiaether:** Coronands containing only sulfur heteroatoms in the ring or crown ether with sulfur instead of oxygen.

Of these terms, the names coronand, crown ether and cryptand are in general usage. All of them can be generally called crown compounds. Our laboratory is involved in the research of selenium crown compounds which we refer to as selenium coronands.

### 1.1.2. Complexation of Crown Compounds

The most striking characteristic of crown compounds is the ability to form complexes. All the research on crown compounds view these structures as possessing heteroatoms and the ability to incorporate cations into their cavities to form stable complexes (Figure 2). During complexation, the cation portion of a metal salt, ammonium salt, or organic ionic compounds (guest) is bound by a crown compound (host) bearing donor atoms such as O, N, S, and Se.



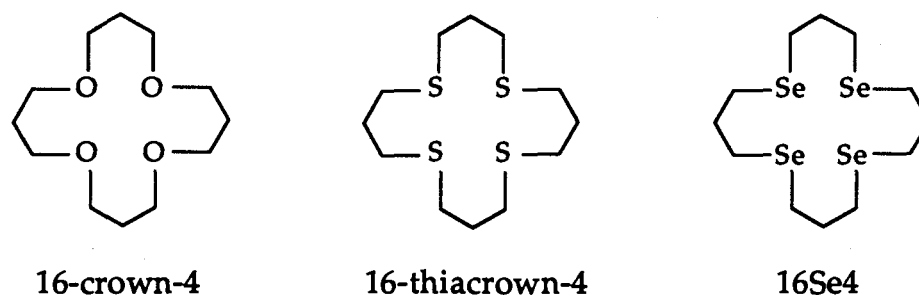
**Figure 2. The complexation between a crown compound and metal ion**

The ability of a crown compound to selectively complex an ion and the stability of the resulting complex depend on the relative diameter of the crown compound's cavity and the diameter of the cation. These properties are also influenced by the charge and "hardness" of the cation, as well as the type of donor atoms present in the crown compound. The donor atoms determine the "hardness" and basicity of the crown compound. In principle, it can be predicted which kinds of metal ions will be bound by certain crown

compounds, based on the factors considered above. So, one should be able to design specific crown compounds for practical uses.

### 1.1.3. Crown Compounds Containing Group VI Elements

Of the many crown compounds, those containing Group VI elements (O, S, and Se) have received most attention. Three typical structures are crown ether (16-crown-4)<sup>[4]</sup>, crown thiaether (16-thiacrown-4)<sup>[5]</sup> and selenium coronand (16Se4), which was synthesized in our laboratory<sup>[3]</sup> (see Fig. 3).



**Figure 3. Typical structures of crown compounds containing Group VI elements.**

These types of compounds, called ionophores, are of great interest due to their selective complexation ability and use as models for the more complex natural host-guest complexes present in antibiotics and membrane transport systems. It can be seen from the above structures, their only difference is the heteroatoms (O, S, Se) in the sixteen membered rings. The hardness and electronegativity of these group VI elements follow the order O

> S > Se. It is the hardness and electronegativity that determine a coronand's selective complexation ability and behavior during complexation<sup>[2]</sup>.

According to the hard-soft acid-base principle, O tends to bind small hard ions, S should bind less hard ions such as transition metal ions, and Se should have a greater tendency to bind large soft metal ions such as Pd<sup>2+</sup>, Pt<sup>2+</sup>, etc<sup>[6]</sup>. The selenium coronand 16Se<sub>4</sub> has also been shown to bind Cu<sup>2+</sup> ion<sup>[7]</sup> which can be classified as a borderline acid<sup>[6]</sup>. The fact is that the oxygen analogs show a high preference for binding alkali and alkaline earth metal cations<sup>[8, 9]</sup>. Some of the transition metal cations and the heavy metal ions form complexes with various crown thiaethers<sup>[10-12]</sup>. Selenium coronands are expected to show similar preferences<sup>[13]</sup>.

#### 1.1.4. Applications of Crown Compounds

Applications of crown compounds are classified according to the functions derived from their specific characteristics, as follows:<sup>[1b]</sup>

(1) Capacity for selective capture, separation, and transport of cations, for example,

- Separation or concentration of alkali or alkaline earth metal ions such as Na<sup>+</sup> - K<sup>+</sup>, Ca<sup>2+</sup> - Sr<sup>2+</sup>, etc<sup>[14a]</sup>.
- Capture, recovery, removal, separation, concentration, or purification of noble or heavy metals such as Ag<sup>+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, etc<sup>[14b]</sup>.
- Separation of lanthanides and actinides<sup>[14c]</sup>.
- Separation of isotopes<sup>[14d]</sup>.
- Ion-selective electrode<sup>[14e]</sup>.

- Ion-transport membrane including liquid membranes<sup>[14f]</sup>.
- Applications to biochemistry and biophysics as synthetic ionophores<sup>[14g]</sup>.
- Applications of physiological activities to agrochemicals and drugs<sup>[14h]</sup>.
- Optical resolution using optically active crown compounds<sup>[14i]</sup>.

(2) Capacity for solubilization of inorganic salts in organic solvents and for the activation of anions, for example

- Inorganic synthesis, such as the synthesis of metal carbonyl derivatives<sup>[14j]</sup>.
- Use in organic synthesis such as phase transfer catalysts<sup>[14k]</sup>.
- Non-aqueous electrochemistry<sup>[14l]</sup>.
- Investigation of the mechanism or kinetics of organic reactions.
- Analytical chemistry<sup>[14m]</sup>.
- Anionic polymerization utilizing the solubilization of alkali metals<sup>[14n]</sup>.
- Investigation of the chemistry of metal ion solutions.

Selenium coronands can act as hosts to bind different metal ions<sup>[7, 13]</sup>. By connecting these selenium coronands to a polymer chain thus forming a polymer with pendant selenium coronands, we expect this polymer to maintain similar complexation properties as single selenium coronands and to have potential uses as a permselective membrane. The research into applications of polymeric selenium coronands will require exploration of the chemistry of polymeric selenium coronands. The latter aspect is the subject of this thesis.

## 1.2. Polymeric Crown Compounds

Most current research on crown compounds is directed towards employing their characteristics for a wide range of applications. However, some problems remain, such as the solubility, biological action, and the toxicity. In addition, the compounds are very expensive for commercial use in the chemical, metallurgical, and atomic power industries, as well as environmental engineering. It is thought that polymeric crown compounds (polymers having crown moieties) or immobilized crown compounds supported on solid carriers might be useful as a means to overcome these problems. Because they are relative stable and long-lasting, insoluble, have very low vapor pressure, it is expected that polymeric crown compounds or immobilized crown compounds will be less expensive and much less toxic than "monomeric" crown compounds. In addition, these polymers may be desirable for industrial usage because they offer advantageous forms for easy treatment, recovery, and reuse, e.g., as membranes or columns for ion-selective separation and powders or granules for catalysts. For these reasons, polymeric and immobilized crown compounds are current subjects of research and significant developments are anticipated.

### 1.2.1. Polymeric Crown Ethers and their Application

One of the most striking features of crown ethers is their selectivity towards the alkali metal cations, which is related to the match between the ionic diameter and the cavity size of the ring. Solid compounds of the crown ethers have been prepared for ion-exchange resins or selective membranes.



Resins with crown ethers have been synthesized by condensation and polymerization reactions.

Polymers have quite different properties from their corresponding monomeric molecules. In recent years, researchers have made efforts to incorporate these crown compounds, such as crown ethers, into polymer backbones to form poly(crown ethers) and to develop applications.

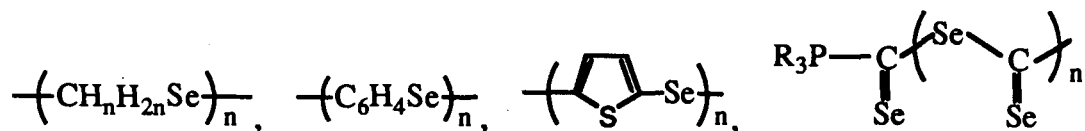
Many kinds of crown ether-containing polymers have been chemically and electrochemically synthesized [15-19], and their complexation properties have been studied[20-30]. These kinds of polymers have been used in areas as diverse as:

- (a) catalysis[24, 25];
- (b) column chromatography[26, 27];
- (c) liquid crystal polymers[28-33];
- (d) solid state electrolytes or ionic conductors[34-36];
- (e) ion diffusion and selectivity[37, 38].

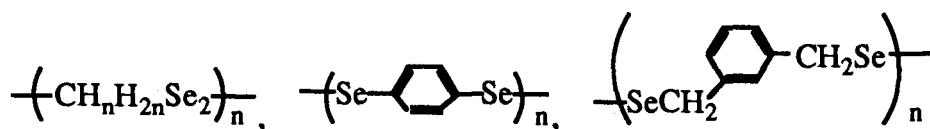
### **1.2.2. Selenium-containing Organic Polymers**

In recent years, high conductive properties of modified polyarylyene sulphides have been observed[39]. The most promising polymer is the commercially available poly(thio-1,4-phenylene). The polymer becomes highly conducting upon exposure to strong oxidants[39]. In addition, a number of selenium-containing polymers, in which selenium atoms are located in the main polymer chain, have been synthesized. They are divided into the following categories[40]:

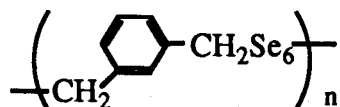
(1) Organoselenium polymers containing a monoselenide chain, such as:



(2) Organoselenium polymers containing a diselenide chain, such as:



(3) Polyselenium-containing polymers, such as:



Although much work has been done on these types of selenium-containing polymers, to date, there have been no reports of polymers with pendant selenium coronands.

### 1.3. Permselectivity and Ion-Selective Electrodes (ISEs)

Ion selective electrodes (ISEs) are a type of device used to quantitatively detect specific ions by means of an interface across which only a single ion can penetrate (this interface is said to have permselectivity). A selectively permeable membrane (e.g. membrane containing ionophores or crown compounds) can be made to form this interface. When the electrode

coated with a permselective membrane is put into a solution containing the specific ion, then the membrane absorbs this specific ion. If this saturated electrode is in contact with a solution that includes the ion, a membrane/solution boundary potential develops (i.e. membrane potential, E).[41]

Neutral carrier type membrane ISEs (membranes employing uncharged chelating agent) have been developed mainly for the detection of alkali and alkaline earth metals. However, continuing investigations into the role of transition metal ion-selective membranes have revealed selenium coronands and poly(selenium crowns) as having the ability to complex transition metal ions<sup>[42, 43]</sup>. The latter have potential applications as new sensor materials in constructing the ISE membrane.

## **1.4. Project Design**

Based on the information given, the research project has been designed as follows:

1. Synthesis of polymers and copolymers containing pendant selenium coronands.
  - a. synthesis of selenium coronands ( $8\text{Se}_2$  or  $16\text{Se}_4$ ) with hydroxyl functional groups.
  - b. covalent attachment of an acryloyl group to the functional group to form selenium coronand monomers.
  - c. free radical polymerization of the monomers.
2. Characterization of these new polymers.

- a. evaluation of the complexation abilities of the polymers with various metal ions and comparison of the results with those for monomeric selenium coronands.
  - b. determination of the electrochemical properties of these polymers using cyclic voltammetry and comparison of the results with those for monomeric selenium coronands.
3. Evaluation of these new polymer materials as permselective membranes for ion-selective electrodes (ISEs).

# Chapter 2

## SYNTHESIS OF POLYMERS

### 2.1. General

Two methods have been used in the preparation of polymeric crown compounds: vinyl polymerization or copolymerization of the vinyl derivatives of crown compounds by free radical or ionic polymerization; polycondensation of crown compounds that have two or more functional groups.

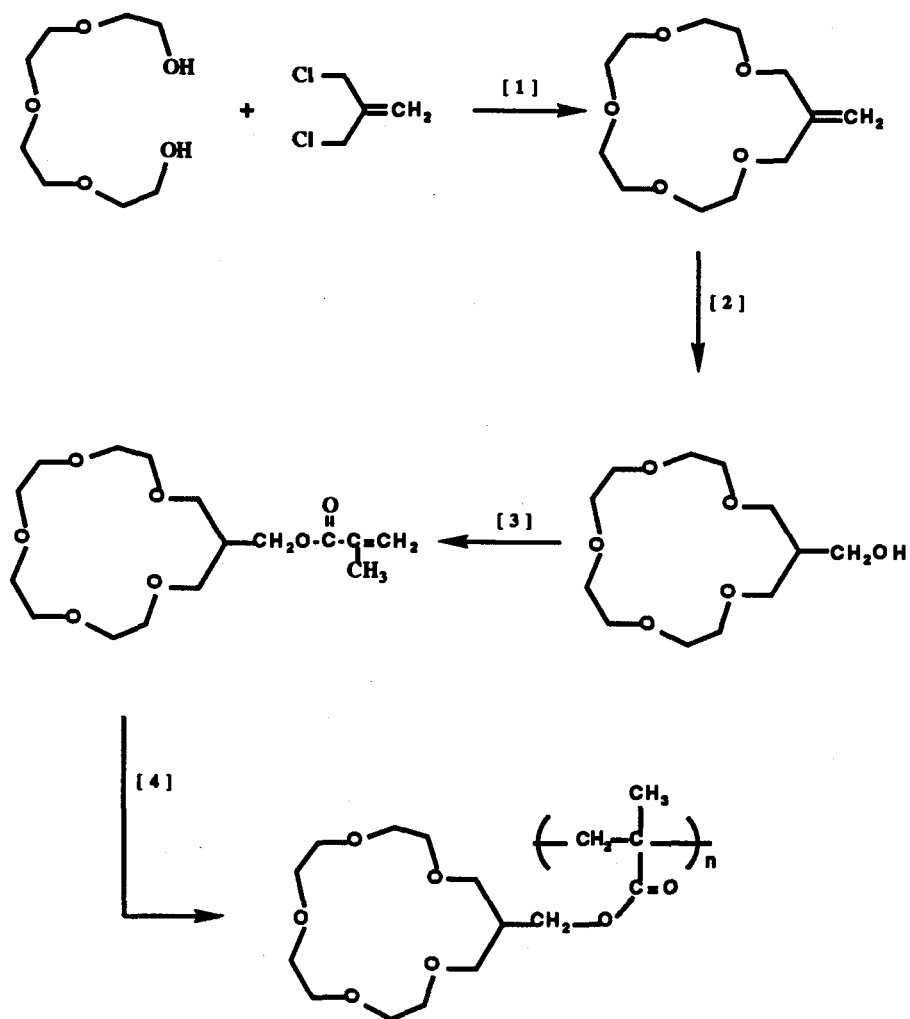
#### 2.1.1. Synthesis of Poly (Vinyl Crown Compounds)

Poly(vinyl crown compounds) have been prepared by the synthesis of monomeric crown compounds having vinyl groups followed either by radical or anionic polymerization to give homopolymers or by copolymerization with a comonomer such as styrene.

Kopolow *et al.* [44-47] have synthesized vinyl derivatives of benzo-15-crown-5, dibenzo-15-crown-5, and dibenzo-18-crown-6, and have prepared homopolymers and copolymers (copolymerized with styrene using a radical initiator of  $\alpha$ -methylstyrene tetramer dianion). Recently, Peramanage *et al.* [34] used a similar method (see Scheme 2-1) to prepare

poly[(hydroxymethyl)-16-crown-5 methacrylate]. The latter is a potential candidate for solid-state electrolytes.

Scheme 2-1



[1] NaH/THF

[3] Methacryloyl chloride/benzene, TEA

[2]  $\text{BH}_3(\text{CH}_3)_2\text{S}/\text{THF}, \text{H}_2\text{O}_2, \text{OH}^-$

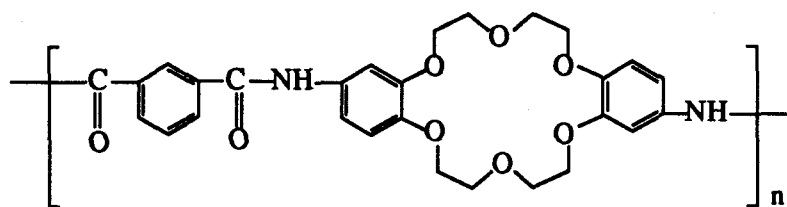
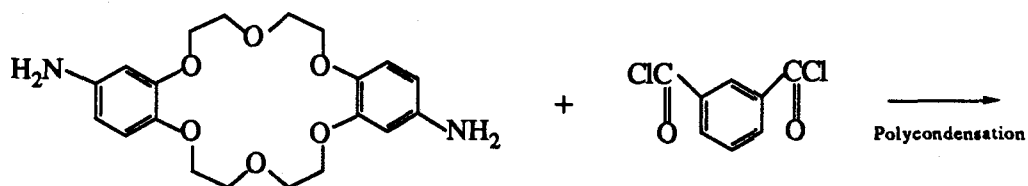
[4] AIBN/60°C

## 2.1. 2. Polymeric Crown Compounds Prepared by Polycondensation

Two classes of polymeric crown compounds have been prepared by polycondensation: those based on polyamides, and those based on polyesters.

Feigenbaum and Michel<sup>[48]</sup> prepared a polyamide with main chain crown ring moieties in the early 1970's. Scheme 2-2 shows the typical synthetic scheme for a crown ether polyamide.

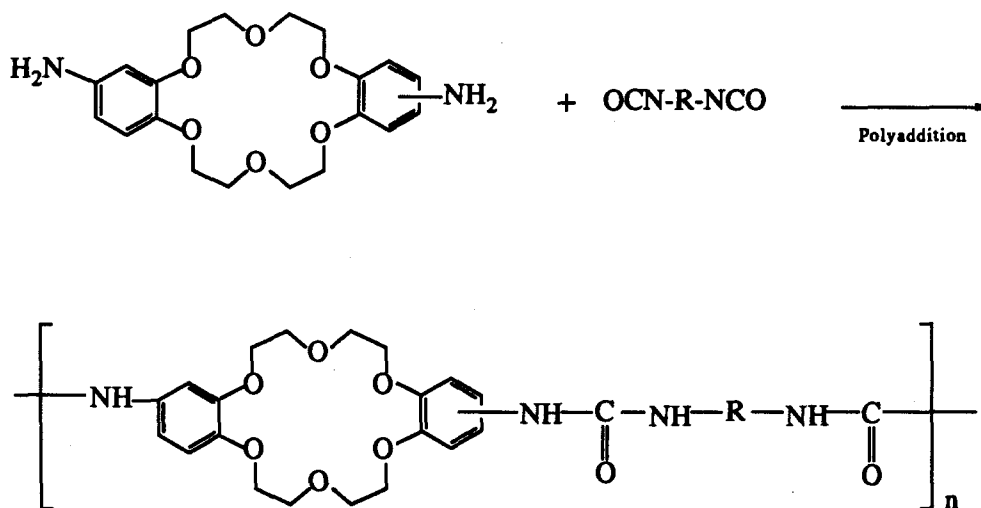
Scheme 2-2



Crown ether polyamide

Crown ether polyureas have been prepared by the polyaddition of a bisisocyanate such as tolylene, diphenylmethane bisisocyanate, or hexamethylene bisisocyanate to yield diaminodibenzo-crown ether, as in Scheme 2-3.[49]

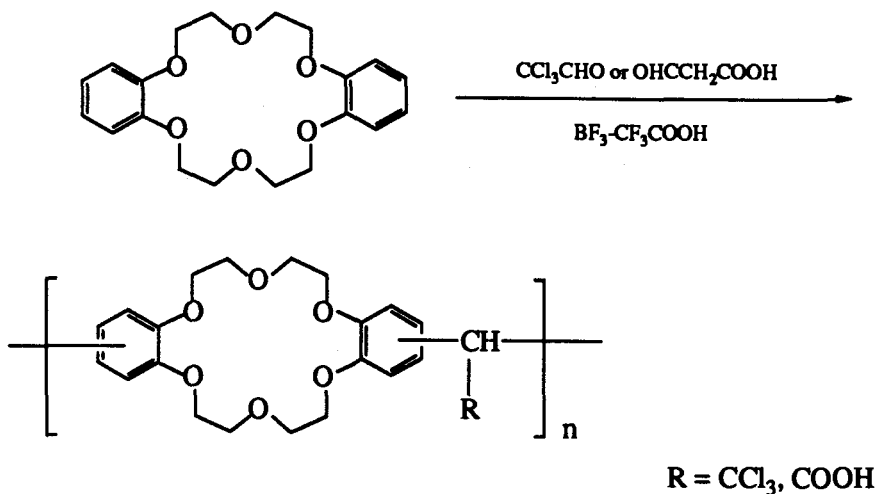
Scheme 2-3



A polymer prepared by the additive condensation of dibenzo-18-crown-6 with chloral or glutaric acid in CF<sub>3</sub>COOH containing BF<sub>3</sub> has also been reported (Scheme 2-4).[50]



### Scheme 2-4

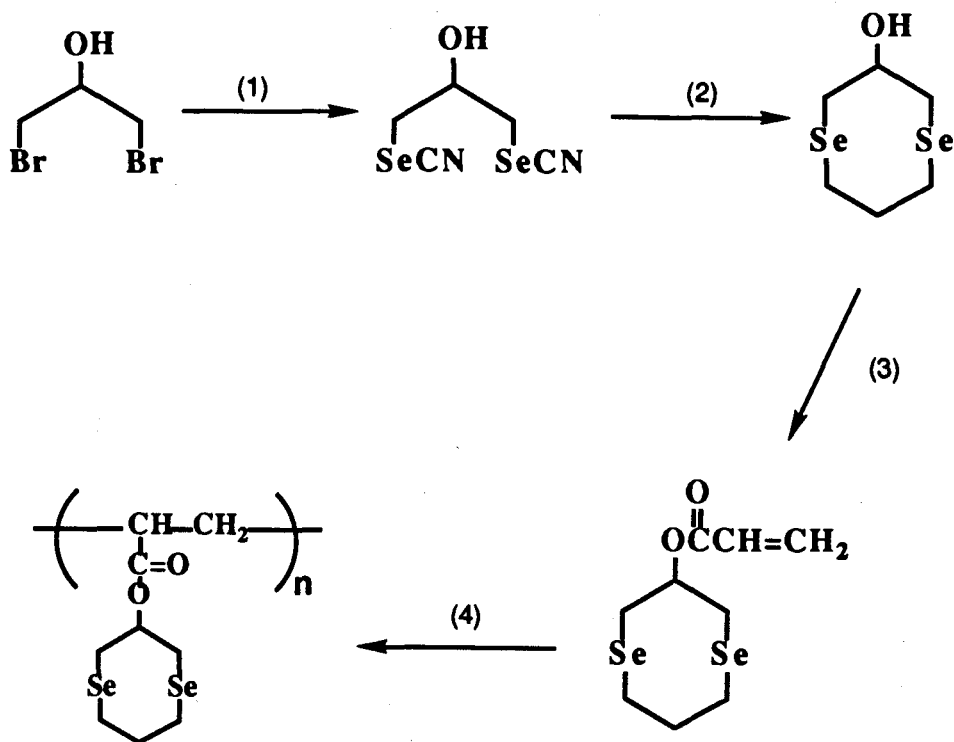


#### 2.1.3. Design of a Synthetic Scheme for Poly (Selenium Coronands)

For the synthesis of polymeric selenium coronands, vinyl polymerization (Scheme 2-1) was selected. The strategy involved the synthesis of a selenium coronand bearing a functional group such as a hydroxyl group, which was subsequently used to connect it to another functional group to form a reactive monomer. An acrylate was chosen as the second functional group due to its facile polymerization.

Polymerization of the monomer afforded the target polymer-poly(selenium coronands). The synthetic route of the simplest polymer, poly8Se2 (PDSA), was as follows:

Scheme 2-5



With the methodology illustrated in Scheme 2-5, the synthesis of a number of different polymers (by changing the vinyl group attached to the coronand or by changing selenium coronands) is possible. In addition, copolymers can be synthesized by the copolymerization of selenium coronand-containing monomers with other reactive monomers.

## 2.2. Experimental

### 2.2.1. General

Infrared spectra were recorded on a Perkin-Elmer 599B Infrared Spectrophotometer. UV-visible absorption spectra were carried out a Perkin-Elmer Lamda 3A UV-visible spectrophotometer.  $^1\text{H}$  NMR (400.13 MHz),  $^{13}\text{C}$  NMR (100.6 MHz) spectra were recorded on a Bruker AMX-400 NMR spectrometer. All NMR spectra were recorded in deuteriochloroform and chemical shifts are given in ppm downfield from TMS. Electron impact ionization mass spectra were recorded on a Hewlett-Packard HP-5985 mass spectrometer. AAS measurements were carried out on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. DSC measurements were performed on a Perkin-Elmer DSC-7/TAC-7 instrument. Average molecular weights of polymers were determined by GPC which included size exclusion chromatography combined with a Spectra-Physics Model SP8000 UV-vis spectrophotometer and a Waters Model R400 refractive index detector. Electrochemical studies were performed on a Pine RDE4 bipotentiostat and a Hewlett-Packard HP 7046A X-Y recorder. Analytical thin-layer chromatography (TLC) was performed on aluminum plates precoated with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, exposed to UV light and /or sprayed with 5% sulfuric acid in ethanol, and heated at 150 °C. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory at Simon Fraser University. Solvents were dried before use, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 50 °C.

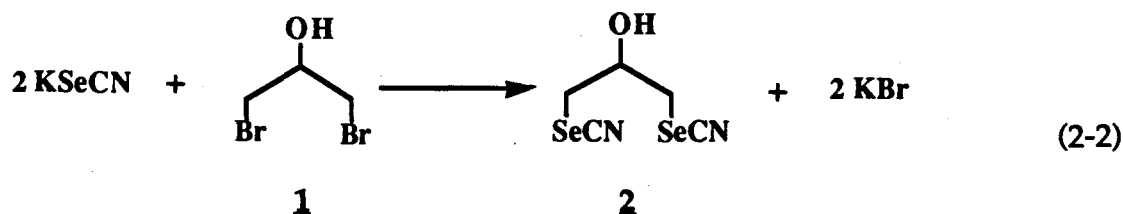
## 2.2.2. Synthesis of Monomeric Selenium Coronands

### Potassium selenocyanate



A mixture of KCN (65.12 g, 1.00 mol) and commercial gray selenium (78.96 g, 1.00 mol) was put into a large porcelain evaporating dish, and was melted gradually to  $\sim 160^\circ\text{C}$  by using an electric hot plate. The melt was stirred with a porcelain spatula until all the selenium had dissolved. The reaction took about two hours. It was then permitted to cool slowly, with continuous stirring in order to prevent caking during solidification. The cold melt was crushed to a fine powder and was immediately dissolved in hot acetone (500 ml). The solution was filtered and the residue was washed with warm acetone. The filtrate was transferred to a distilling flask, and two-thirds of the acetone was distilled off. The remaining solution was poured into a beaker, where a large part of the salt separated on cooling. The colorless needles were filtered and washed several times with anhydrous ether. The remaining ether was removed under vacuum. Yield: 118.1g, 82%. m.p.  $99^\circ\text{C}$ ; lit.[64]  $99^\circ\text{C}$ .

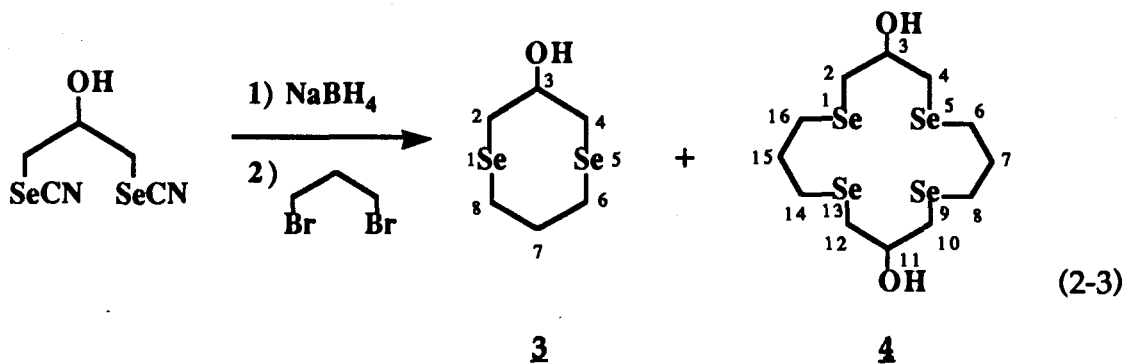
### 1,3-Propanebisseleno-cyanate-2-ol **2**



In a three-necked round bottom flask, KSeCN (3.00 g, 0.021 mol) and dry acetone (30 ml) were added. Then 1,3-dibromopropan-2-ol **1** (2.18 g, 0.01 mol) was added to the flask with stirring at room temperature. The reaction mixture was heated at reflux and stirred for 16 h.

The mixture was filtered to remove most of the KBr and the filtrate was distilled to remove all acetone. The residue was a yellow-reddish oil (3.20 g). This product was purified by chromatography in a silica-gel column with a mixture of ethyl acetate-hexane (1 : 1) as eluent ( $R_f = 0.45$ ). The fractions containing pure 1,3-propanebisselenocyanate-2-ol **2** were combined and the solvent removed to give the product as an oil (2.58 g, 96%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 3.29 (2H,  $\text{SeCH}_2$ , m), 3.59 (1H, OCH, m), 4.32 (1H, OH, s); Anal. Calcd (found) for  $\text{C}_5\text{H}_6\text{N}_2\text{OSe}_2$ : C, 22.40 (22.54); H, 2.25 (2.44); N, 10.40 (10.15); m.p. 43.5°C.

**3-Hydroxy-1,5-diselenacyclooctane 3 and 3, 11- dihydroxy-1,5,9,13-tetraselenacyclohexadecane 4**



1,3-Propanebisselenocyanate-2-ol **2** (2.50 g, 0.093 mol) was dissolved in dry THF (220 ml) and EtOH (25 ml) and put into a three-necked round

bottom flask. Sodium borohydride (3.5 g, 0.093 mol) was added in small portions at room temperature until the solution became yellowish white. The mixture was stirred for a few minutes. 1, 3-Dibromopropane (2.03 g, 0.010 mol) was dissolved in a mixture of THF and EtOH (1 : 1) (70 ml) and added dropwise to the reaction flask over 2 h. The reaction mixture was stirred at room temperature for 20 h. All processes were carried out under N<sub>2</sub>.

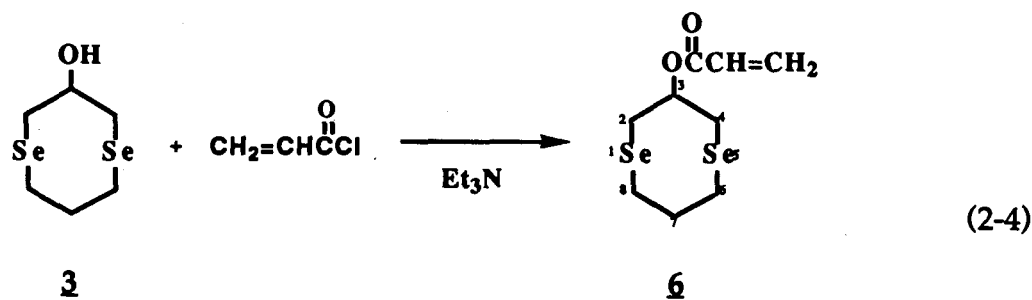
The reaction mixture was filtered and the filtrate was placed on a rotary evaporator to remove most of the solvent. Water (100 ml) was added to the residue and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 120 ml CH<sub>2</sub>Cl<sub>2</sub>). The organic layers were combined, washed with water (3 × 100 ml H<sub>2</sub>O) and dried with MgSO<sub>4</sub>. Removal of the CH<sub>2</sub>Cl<sub>2</sub> gave a crude yellow oil (2.90 g). The products were separated on a silica-gel column with a mixture of ethyl acetate-hexane (1 : 3.5) as eluent. The fractions with R<sub>f</sub>: 0.43 were combined to yield **3** as an oil (1.04 g, 43%) and those with R<sub>f</sub>: 0.10 were combined to give **4** as a white solid (0.54 g, 11%), <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: **3** 2.23 (1H, OH, s), 2.40 (2H, H<sub>7</sub>, m), 2.75 (4H, H<sub>6</sub>, H<sub>8</sub>, m), 3.07 (4H, H<sub>2</sub>, H<sub>4</sub>, m), 3.95(1H, H<sub>3</sub>, m); Anal. Calcd (found) for C<sub>6</sub>H<sub>12</sub>OSe<sub>2</sub>: C, 27.92 (28.19); H, 4.69 (4.87). **4** 1.58 (2H, OH, s), 2.06 (4H, H<sub>7</sub>, H<sub>15</sub>, m), 2.67-2.78(16H, H<sub>2</sub>, H<sub>4</sub>, H<sub>6</sub>, H<sub>8</sub>, H<sub>10</sub>, H<sub>12</sub>, H<sub>14</sub>, H<sub>16</sub>, m), 3.83 (2H, H<sub>3</sub>, H<sub>11</sub>, m); Anal. Calcd (found) for C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>Se<sub>4</sub> : C, 27.92 (28.24); H, 4.69 (4.75).

### 3-Hydroxy-1,5,9,13-tetraselenacyclohexadecane **5**

This compound was prepared by Dr. Ivan Cordova and was obtained as a white solid.<sup>[51]</sup>

### 2.2.3. Synthesis of Functionalized Monomers

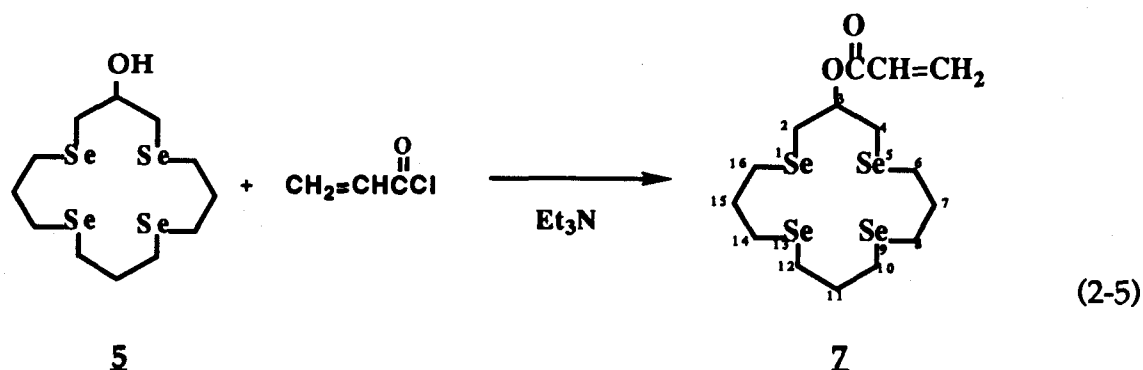
#### 1,5-Diselenacyclooctyl acrylate (mono8Se2) **6**



3-Hydroxy-1,5-diselenacyclooctane (8Se2-OH) (0.64g, 0.002 mol) was dissolved in dry THF (190 ml) and  $\text{CH}_2\text{Cl}_2$  (10 ml). The solution was cooled in ice and triethylamine (1.52 g, 0.015 mol) was added. Acryloyl chloride (0.24g, 0.0026 mol) was dissolved in THF (30 ml) and added dropwise with vigorous stirring over 17 min to the reaction mixture. The reaction mixture was stirred overnight at room temperature. Triethylammonium salts were removed by filtration, and the filtrate containing mono8Se2 was evaporated until most of the solvent was removed. The residue was dissolved in dichloromethane (100 ml). The organic solution was first washed with a mixture of 1 M HCl (15 ml) and  $\text{H}_2\text{O}$  (45 ml), then with a mixture of saturated  $\text{NaHCO}_3$  (5 ml) and  $\text{H}_2\text{O}$  (45 ml), and finally with  $\text{H}_2\text{O}$  (3 x 150 ml). The organic layer was dried with  $\text{MgSO}_4$ , and removal of the solvent afforded crude mono8Se2 as a straw-colored oil. The product was chromatographed on a silica-gel column with a mixture of ethyl acetate-hexane (1:20). The fractions containing pure **6** ( $R_f = 0.3$ ) were combined, and the product was isolated as a thick oil by removal of the solvent (0.67 g, 87%).

IR (KBr),  $\text{cm}^{-1}$ : 1710 ( $\nu_{\text{C=O}}$ ), 1180 ( $\nu_{\text{C-O-C}}$ ); MS: 312 ( $\text{M}^+$ ); UV,  $\lambda_{\text{max}}$ : 234nm ( $\epsilon$   $3.10 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$ );  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 2.40 (2H,  $\text{H}_7$ , m), 2.83 (4H,  $\text{H}_6$ ,  $\text{H}_8$ , m), 3.15 (4H,  $\text{H}_2$ ,  $\text{H}_4$ , m), 5.23 (1H,  $\text{H}_3$ , m), 5.83 (1H,  $-\text{HC}=\text{CH}_z$ , dd,  $J_{\text{H-H}_z} = 10.5 \text{ Hz}$ ,  $J_{\text{gem}} (\text{H}_z/\text{H}_E) = 1.5 \text{ Hz}$ ), 6.09 (1H,  $-\text{HC}=\text{CH}_z$ , dd,  $J_{\text{H-H}_E} = 17.5 \text{ Hz}$ ,  $J_{\text{H-H}_z} = 10.5 \text{ Hz}$ ), 6.39 (1H,  $-\text{HC}=\text{CH}_E$ , dd,  $J_{\text{gem}} (\text{H}_z/\text{H}_E) = 1.5 \text{ Hz}$ ,  $J_{\text{H-H}_E} = 17.5 \text{ Hz}$ );  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 24.2 ( $\text{C}_7$ ), 26.6 ( $\text{C}_6$ ,  $\text{C}_8$ ), 30.9 ( $\text{C}_2$ ,  $\text{C}_4$ ), 73.8 ( $\text{C}_3$ ), 128.5 ( $=\text{CH}_2$ ), 130.9 ( $\text{CO}-\text{CH}=\text{}$ ), 165.0 ( $-\text{C}=\text{O}$ ); Anal. Calcd (found) for  $\text{C}_9\text{H}_{14}\text{O}_2\text{Se}_2$ : C, 34.65 (34.69); H, 4.52 (4.48).

### 1,5,9,13-Tetraselenacyclohexadecyl acrylate (mono16Se4) **7**



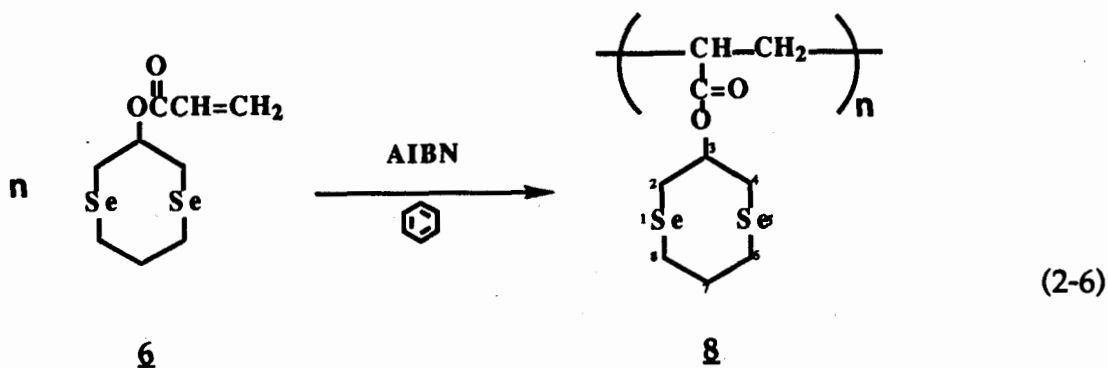
3-Hydroxy-1,5,9,13-tetraselenacyclohexadecane (16Se4-OH) **5** [51] (0.125g, 0.25 mmol) was dissolved in dry THF (20 ml) and  $\text{CH}_2\text{Cl}_2$  (10 ml). The solution was cooled in ice and triethylamine (0.030 g, 0.300 mmol) was added. Acryloyl chloride (0.24g, 0.0026 mol) was dissolved in THF (20 ml) and added dropwise with vigorous stirring over 10 min to the reaction mixture. The reaction mixture was stirred overnight at room temperature. Triethylammonium salts were removed by filtration, and the filtrate containing mono16Se4 was evaporated until most of the solvent was removed. The residue was dissolved in dichloromethane (60 ml). The



organic solution was first washed with a mixture of 1 M HCl (15 ml) and H<sub>2</sub>O (30 ml), then with a mixture of saturated NaHCO<sub>3</sub> (5 ml) and H<sub>2</sub>O (30 ml), and finally with H<sub>2</sub>O (3 x 100 ml). The organic layer was dried with MgSO<sub>4</sub>, and removal of the solvent afforded crude mono<sup>16</sup>Se<sub>4</sub> as a straw-colored oil. The product was chromatographed on a silica-gel column with a mixture of ethyl acetate-hexane (1:20) as the eluent. The fractions containing pure Z (R<sub>f</sub> = 0.15) were combined, and the product was isolated as a thick oil by removal of the solvent (0.10 g, 75%). IR (KBr), cm<sup>-1</sup>: 1718 (ν<sub>C=O</sub>), 1180 (ν<sub>C-O-C</sub>); MS: 554 (M<sup>+</sup>); UV, λ<sub>max</sub>: 246nm (ε 4.92x10<sup>3</sup> cm<sup>-1</sup>M<sup>-1</sup>); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 2.00-2.30(6H, H<sub>7</sub>, H<sub>11</sub>, H<sub>15</sub>, m), 2.65-2.85 (12H, H<sub>6</sub>, H<sub>8</sub>, H<sub>10</sub>, H<sub>12</sub>, H<sub>14</sub>, H<sub>16</sub>, m), 2.85-3.05 (4H, H<sub>2</sub>, H<sub>4</sub>, m), 5.15 (1H, H<sub>3</sub>, m), 5.86 (1H, -HC=CH<sub>Z</sub>, dd, J<sub>H-H<sub>Z</sub></sub> = 10 Hz, J<sub>gem</sub> (H<sub>Z</sub>H<sub>E</sub>) = 2 Hz), 6.13 (1H, -HC=CH<sub>2</sub>, dd, J<sub>H-H<sub>E</sub></sub> = 17 Hz, J<sub>H-H<sub>Z</sub></sub> = 10Hz), 6.44 (1H, -HC=CH<sub>E</sub>, dd, J<sub>gem</sub> (H<sub>Z</sub>H<sub>E</sub>) = 2 Hz, J<sub>H-H<sub>E</sub></sub> = 17 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>), δ<sub>ppm</sub>: 23.5 (C<sub>11</sub>), 23.7(C<sub>7</sub>, C<sub>15</sub>), 24.7 (C<sub>10</sub>, C<sub>12</sub>), 27.1( C<sub>6</sub>, C<sub>8</sub>, C<sub>14</sub>, C<sub>16</sub>), 31.6 (C<sub>2</sub>), 31.8 (C<sub>4</sub>), 73.7 (C<sub>3</sub>), 128.2 (=CH<sub>2</sub>), 131.2 (CO-CH=), 165.4 (-C=O); Anal. Calcd (found) for C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>Se<sub>4</sub>: C, 32.51 (32.79); H, 4.73 (4.87).

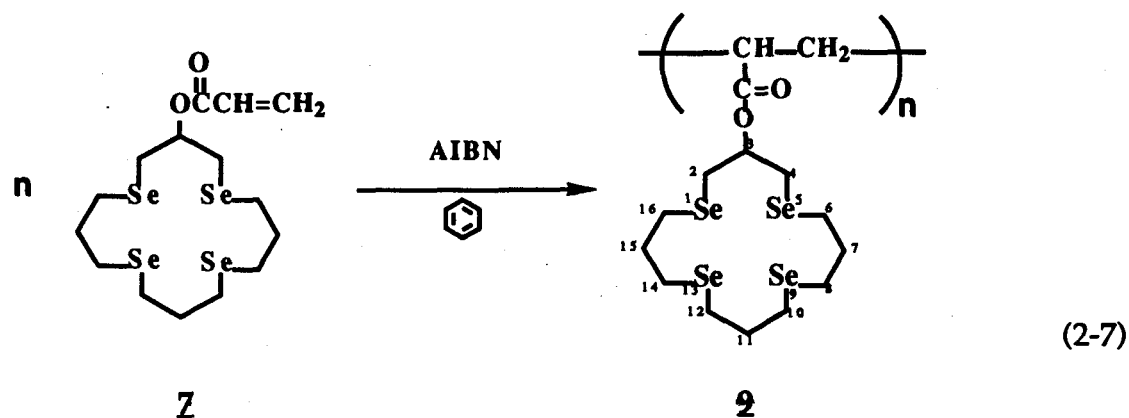
#### 2.2.4. Synthesis of Polymers

##### Poly(1,5-diselenacyclooctyl acrylate) (Poly8Se2) **8**



Mono8Se2 **6** (0.20 g, 0.64 mmol) and AIBN (5% mole ratio to the monomer) were dissolved in benzene (0.80 g, 10.3 mmol). This solution was placed in a glass ampoule and degassed in three freeze-thaw cycles, sealed under vacuum and heated for 110 hrs at 60°C (equation 2-6). The solution was then poured into MeOH (7 ml) and the polymer was precipitated (0.20 g). The polymers were purified by three dissolution-precipitation steps from chloroform-methanol. Yield: 0.18g, 90%; IR (KBr),  $\text{cm}^{-1}$ : 1705( $\nu_{\text{C=O}}$ ), 1155( $\nu_{\text{C-O-C}}$ ); UV,  $\lambda_{\text{max}}$ : 244nm ( $\epsilon$ :  $9.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ );  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 1.46, 1.64, 1.88 (two diastereotopic methylene protons in the backbone,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.27 (1H,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.40 (2H,  $\text{H}_7$ , br.), 2.85 (4H,  $\text{H}_6$ ,  $\text{H}_8$ , br.), 3.15 (4H,  $\text{H}_2$ ,  $\text{H}_4$ , br.), 5.16 (1H,  $\text{H}_3$ , br.),  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 24.4 ( $\text{C}_7$ ), 26.6, 26.8 ( $\text{C}_6$ ,  $\text{C}_8$ ,  $\text{CO}-\text{CH}-\text{CH}_2$ ), 31.0( $\text{C}_2$ ,  $\text{C}_4$ ), 41.5 ( $\text{CO}-\text{CH}-\text{CH}_2$ ), 74.5 ( $\text{C}_3$ ), 173.4 ( $-\text{C}=\text{O}$ ). GPC (Gel Permeation Chromatography) gave the average molecular weight of the soluble fraction as 2500. Anal. Calcd (found) for  $(\text{CH}_3)_2(\text{CN})\text{C}-(\text{C}_9\text{H}_{14}\text{O}_2\text{Se}_2)_n-\text{C}(\text{CN})(\text{CH}_3)_2$ ,  $n=7.577$  : C 36.57 (35.07), H 4.72 (4.44), N 1.12 (1.16).

**Poly(1,5,9,13-tetraselenacyclohexadecyl acrylate) (Poly16Se4) **9****

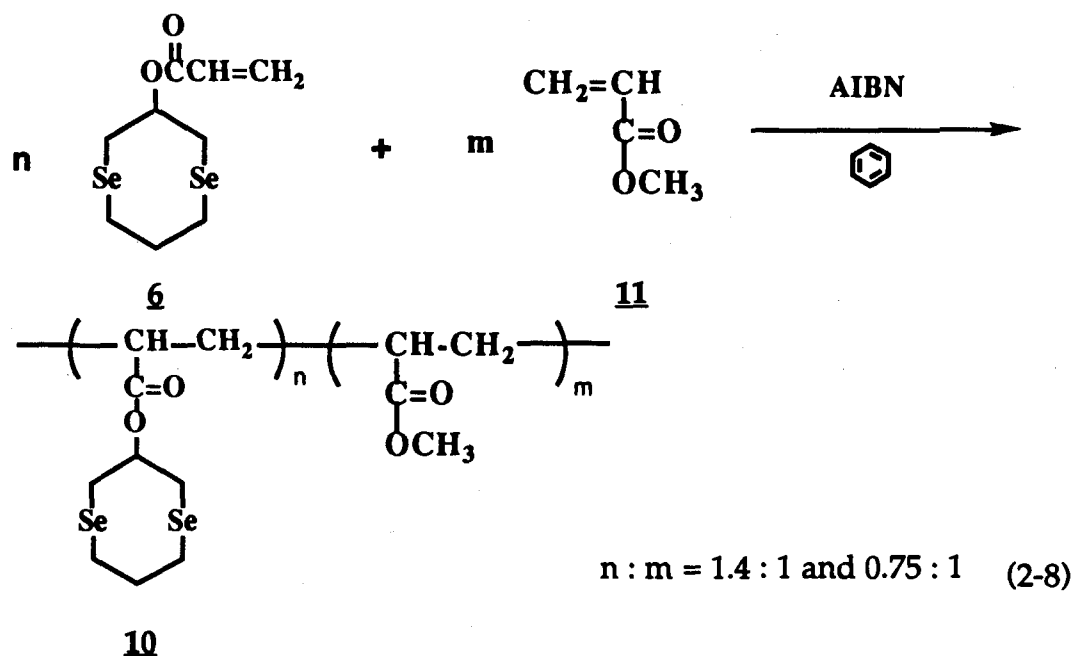


Mono16Se4 **2** (100 mg, 0.18 mmol) and AIBN (5% mole ratio to the monomer) were dissolved in benzene (0.40 g, 5.1 mmol). This solution was placed in a glass ampoule and degassed in three freeze-thaw cycles, sealed under vacuum and polymerized for 110 hrs at 60°C (equation 2-7). The solution was then poured into MeOH (7 ml) and the polymer was precipitated (0.20 g). The polymers were purified by three dissolution-precipitation steps from chloroform-methanol. Yield: 94.8mg, 95%; IR (KBr),  $\text{cm}^{-1}$ : 1728( $\nu_{\text{C=O}}$ ), 1156( $\nu_{\text{C-O-C}}$ ); UV,  $\lambda_{\text{max}}$ : 246nm ( $\epsilon$   $3.90 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$ );  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 1.70-2.13 (two diastereotopic methylene protons in the backbone,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 1.95-2.19 (6H,  $\text{H}_7$ ,  $\text{H}_{11}$ ,  $\text{H}_{15}$ , br.), 2.50 (1H,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.63-2.80 (12H,  $\text{H}_6$ ,  $\text{H}_8$ ,  $\text{H}_{10}$ ,  $\text{H}_{12}$ ,  $\text{H}_{14}$ ,  $\text{H}_{16}$ , br.), 2.80-3.20 (4H,  $\text{H}_2$ ,  $\text{H}_4$ , br.), 5.10 (1H,  $\text{H}_3$ , br.);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 23.8 ( $\text{C}_7$ ,  $\text{C}_{11}$ ,  $\text{C}_{15}$ ), 24.8 ( $\text{C}_{10}$ ,  $\text{C}_{12}$ ), 27.0( $-\text{CO}-\text{CH}-\text{CH}_2$ ) 27.1( $\text{C}_6$ ,  $\text{C}_8$ ,  $\text{C}_{14}$ ,  $\text{C}_{16}$ ), 31.4( $\text{C}_2$ ), 31.8 ( $\text{C}_4$ ), 41.5 ( $\text{CO}-\text{CH}-\text{CH}_2-$ ), 73.7 ( $\text{C}_3$ ), 173.5 ( $-\text{C}=\text{O}$ ). Anal. Calcd (found): C 34.64 (32.65), H 4.95 (4.79).

Both **8** and **9** have lower experimental carbon values than the calculated ones in their microanalyses. This may be because our calculation is based on the products from the polymerization terminated through radical coupling, which have two terminal  $(\text{CH}_3)_2(\text{CN})\text{C}-$  groups. Disproportionation may also occur during the termination process of a free radical polymerization, which gives a product with only one terminal  $(\text{CH}_3)_2(\text{CN})\text{C}-$  group (i.e. four C atoms less). The carbon value of this product is lower than the product with two terminal groups. The experimental carbon value therefore results from a mixture of products having one or two terminal  $(\text{CH}_3)_2(\text{CN})\text{C}-$  groups.

## 2.2.5. Synthesis of Copolymer

### Copolymer of 1,5-diselenacyclooctyl acrylate **6** and methyl acrylate **11**



Methyl acrylate **11** (25 g, 0.29 mol) was washed three times with 1.0 M aqueous NaOH (20 ml x 3) until free from inhibitors (e.g. hydroquinone), then washed with distilled water (30 ml x 3), dried with  $\text{CaCl}_2$  and fractionally distilled under reduced pressure. The product was sealed under nitrogen and stored at low temperature in the dark for later use.

Methyl acrylate **11** (25.8 mg, 0.3 mmol), mono8Se2 **6** (93.6 mg, 0.3 mmol) and AIBN (4.92 mg, 0.015 mmol) were added to benzene (478 mg, 6.1 mmol). The solution was degassed with three freeze-thaw cycles, sealed under vacuum and heated for 110 hrs at  $60^\circ\text{C}$ . The solution was then poured into MeOH (20 ml) and the polymer, Cop8Se2-A **10** precipitated. The polymer was

purified by three dissolution-precipitation steps from chloroform-methanol. yield: 98.3mg, 82.4%. IR (KBr),  $\text{cm}^{-1}$ : 1706( $\nu_{\text{C=O}}$ ), 1165( $\nu_{\text{C-O-C}}$ ); UV,  $\lambda_{\text{max}}$ : 240nm ( $\epsilon$   $4.50 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$ );  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 1.46, 1.66, 1.92 (two diastereotopic methylene protons in the backbone,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.28 (1H,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.40 (2H,  $\text{H}_7$ , br.), 2.84 (4H,  $\text{H}_6$ ,  $\text{H}_8$ , br.), 3.12 (4H,  $\text{H}_2$ ,  $\text{H}_4$ , br.), 3.67 (3H,  $\text{OCH}_3$ , br.), 5.14 (1H,  $\text{H}_3$ , br.).

Under the same reaction conditions (equation 2-8), Cop8Se2-B was obtained by the polymerization of a mixture of methyl acrylate **11** (34.4 mg, 0.40 mmol), mono8Se2 **6** (62.4 mg, 0.2 mmol), AIBN (4.92 mg, 0.015mmol) and benzene (387 mg, 5.0 mmol). Yield: 82.7mg, 85.5%. IR (KBr),  $\text{cm}^{-1}$ : 1708( $\nu_{\text{C=O}}$ ), 1167( $\nu_{\text{C-O-C}}$ ); UV,  $\lambda_{\text{max}}$ : 239nm ( $\epsilon$   $5.00 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$ );  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 1.46, 1.64, 1.91 (two diastereotopic methylene protons in the backbone,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.27 (1H,  $-\text{CH}_2-\text{CH}-\text{CO}$ , br.), 2.38 (2H,  $\text{H}_7$ , br.), 2.82 (4H,  $\text{H}_6$ ,  $\text{H}_8$ , br.), 3.11 (4H,  $\text{H}_2$ ,  $\text{H}_4$ , br.), 3.65 (3H,  $\text{OCH}_3$ , br.), 5.14 (1H,  $\text{H}_3$ , br.).

# Chapter 3

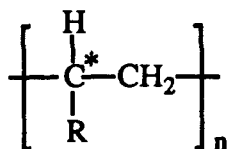
## CHARACTERIZATION OF POLYMERS

The polymers were characterized by some common techniques such as  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and IR spectroscopy, and mass spectrometry. In addition, several other techniques such as GPC, DSC, UV-vis, AAS and CV were applied to the analysis of polymer structures. The following is a discussion of the results based on these analyses.

### 3.1. Structural Analysis of Polymers with Pendant Selenium Coronands

#### 3.1.1. $^1\text{H}$ NMR Spectra of Poly(Selenium Coronands)

The polymerization of an alkene analogue involves the formation of chains whose stereochemical structures depend on the nature of the monomer, the method of polymerization and the reaction conditions<sup>[55-58]</sup>. One of the most common structures of this class of polymer is shown in Fig. 4. The simplest case is the polymerization of ethylene to form polyethylene Fig. 4a. The result is a chain of  $\text{CH}_2$  groups in which all the protons are equivalent.



a: R = H; b: R = CH<sub>3</sub>;

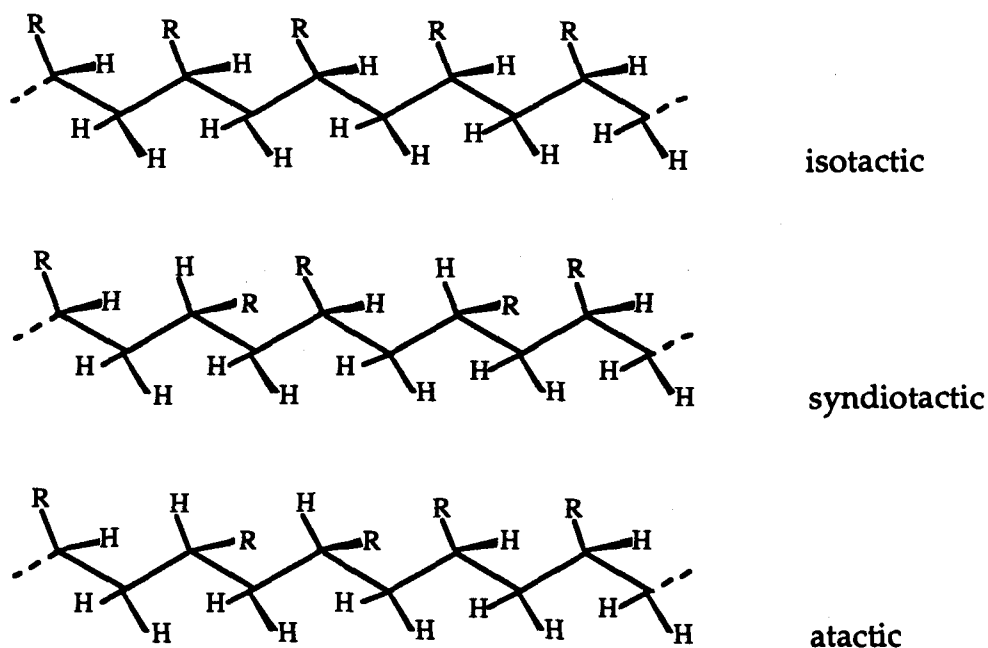
c: R = -COOR', R' = 8Se<sub>2</sub>, 16Se<sub>4</sub>

**Figure 4.** General polymer structure from polymerization of alkene analogues.

For polymers which possess pseudo-asymmetric carbon atoms, the structures and the spectra are more complicated. Examples of such polymers are polypropylene **4b**, and two poly8Se<sub>2</sub> and poly16Se<sub>4</sub> **4c** synthesized in this study. For these polymers, three different types of stereochemical structures are possible. The incorporation of successive monomer units can take place with the same configuration (isotactic chains), or with a regularly alternating configuration (syndiotactic chains), or with random segments of configuration (atactic chains). These stereochemical formulas are shown in Fig. 5 and it can be concluded that these three structural types will give different characteristic NMR spectra. Usually, the CH<sub>2</sub> resonances lie between 1.50 ppm and 2.50 ppm. For the isotactic polymer, the two methylene protons are diastereotopic and give an AX-type spectrum. For the syndiotactic polymer, all the methylene protons are equivalent and give a single peak around 2.00 ppm. For the atactic polymer, the spectra will be a mixture of the two types, with intensities that correspond to their relative proportions.

The <sup>1</sup>H NMR spectra of poly8Se<sub>2</sub> and the mono8Se<sub>2</sub> (Fig. 6) clearly show that the vinyl hydrogens of mono8Se<sub>2</sub> (5.70 ppm to δ6.50 ppm) disappear after the polymerization. Several new signals, associated with backbone

hydrogens of the polymer chain, appear in the region 1.40 ppm to 2.30 ppm. For poly8Se2, the peak at 2.27 ppm is assigned to (underlined H)  $-\text{CO}-\underline{\text{CH}}-\text{CH}_2-$  of the polymer backbone and the peaks at 1.46 ppm, 1.64 ppm and 1.88 ppm belong to the two diastereotopic methylene protons ( $-\text{CO}-\text{CH}-\underline{\text{CH}_2}$ ). The complexity of these signals indicates that the structure of the poly8Se2 is an atactic polymer. Poly16Se4 shows similar situation as poly8Se2 (Fig. 7). Also, the atactic configuration is assigned to copolymers based on their  $^1\text{H}$  NMR spectra.



**Figure 5. Stereochemical formulas showing isotactic, syndiotactic and atactic chains.**

### 3.1.2. DSC of Polymers and Copolymers

Differential scanning calorimetry (DSC) is the dominant technique for the thermal analytical investigation of polymeric materials<sup>[59, 60]</sup>. It measures



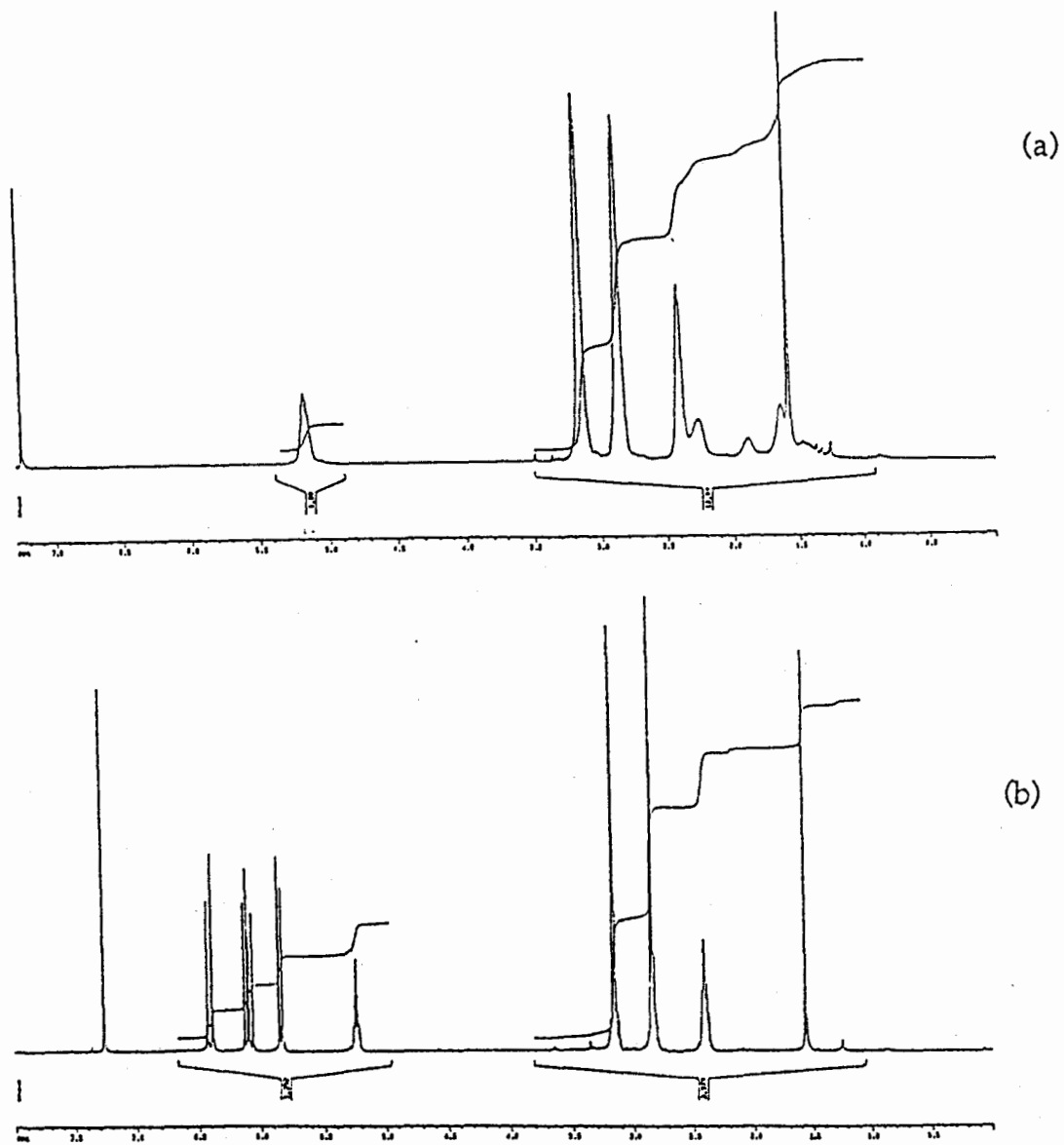


Figure 6.  $^1\text{H}$  NMR (400 MHz) spectra of (a) poly8Se2 and (b) mono8Se2

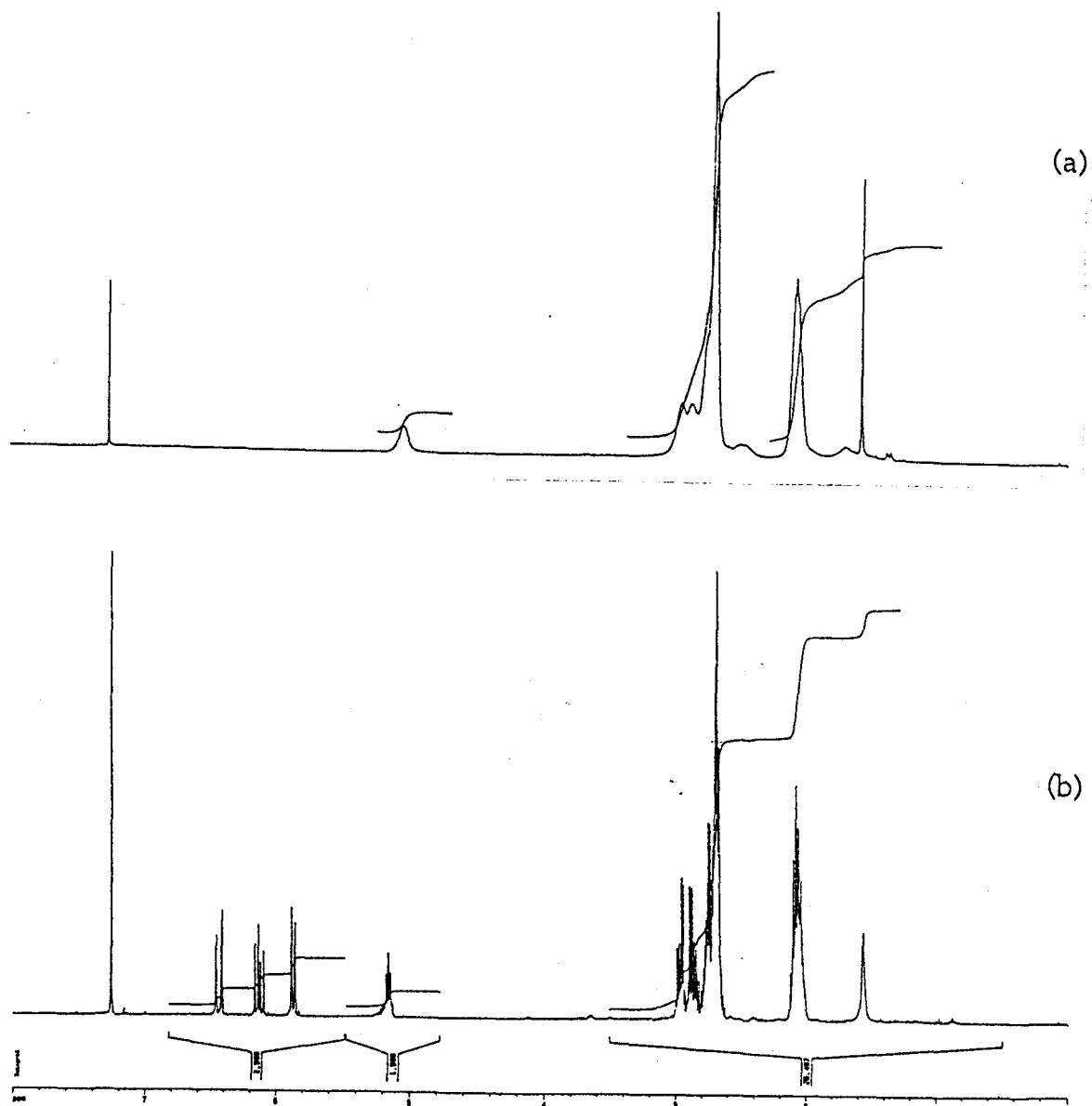


Figure 7.  $^1\text{H}$  NMR (400 MHz) spectra of (a) poly16Se4 and (b) mono16Se4

the difference in energy inputs into a substance and a reference material as they are subjected to a controlled temperature program. Practically all physical and chemical processes involve changes in enthalpy or specific heat, and the applicability of DSC to condensed-phase systems is almost universal. Its measurement process is quantitative and the change of enthalpy is usually a linear function of the reaction coordinate.

**Table 1. The melting and decomposition peak temperatures of polymers and copolymers**

Sample	Poly8Se2	Cop8Se2-A	Cop8Se2-B	Poly16Se4
Melting ( $T_m$ , °C)	78.8	71.5	27.6	95.3
Decomposition (°C)	208.1	216.3	218.0	233.2

DSC studies for the polymers, copolymers and polymer-salt complex were carried out within the temperature span range 25 to 270 °C. In this temperature region, it was found only endothermic melting peaks and decomposition peaks for polymers and copolymers occurred. The temperatures corresponding to these peaks are listed in Table 1. Poly16Se4 has a higher  $T_m$  than poly8Se2 because the former polymer has larger branching coronands-16Se4 on the chain and this makes the chain hard to move. In the situation of poly8Se2 and the copoly8Se2,  $T_m$  is decreased as more small OCH<sub>3</sub> groups are inserted on the chain, separating the 8Se2 coronands. More flexibility and less crystallinity of the chains, lower the melting points. All the polymers and copolymers decomposed at temperatures above 200 °C. Cop8Se2-A/B decomposed at a little higher

temperature than that of poly8Se2 probably because the crowded 8Se2 in the poly8Se2 produces a steric constraint and makes the polymer relatively unstable as compared to the copolymers. After the decomposition of polymers and the copolymers, a strong selenium odor could be detected.

### 3.1.3. Gel Permeation Chromatography

Gel permeation chromatography also called size exclusion chromatography, is a standard method of polymer characterization. The main area of application is the separation of polydisperse substances into monodisperse fractions of different molecular weights. The smaller the molecules, the deeper they penetrate into the pores of the gel. Therefore, larger molecules are eluted before smaller ones<sup>[61, 62]</sup>. The eluted molecules are examined by the detectors. There are usually two kinds of detectors: RI detectors, which measure the difference of the refractive index between solution and pure solvent; UV detectors, which measure the UV absorption of the molecules in the range from 200 to 600 nm.

In the experiment for poly8Se2, both detectors were used. GPC gives an elution chromatogram which correlates the molecular weight distribution with retention time. The peak maximum (retention time = 28.20 mins) correlates with an average molecular weight of 2500 (about 7 ~ 8 repeating units on each chain) for the soluble components in THF with a range of retention time from 23.40 to 31.45 mins. However, a large fraction (> 50%) of the polymer was insoluble in THF due to its having a larger molecular weight. Thus the average molecular weight is higher than 2500 but the actual value is unknown at present.

## 3.2. Interaction of Poly(Selenium Coronands) with Metal Ions

### 3.2.1. UV-visible Study of the Polymer Interaction with Metal Ions

Absorption of ultraviolet or visible light by a molecule results in electronic transitions, e. g., promotion of electrons from low-energy, ground-state orbitals to higher-energy excited-state orbitals.<sup>[63]</sup> When a selenium coronand forms a complex with metal ions, the molecule absorbs radiation at longer wavelength. This transition may involve the promotion of electrons from the bonding orbital between selenium and the metal ion to the empty d orbital of the metal ion (charge-transfer band). In the case of poly8Se2, it is also possible that the absorption may be due to the uncomplexed selenium coronand dication which is produced from the interaction between metal ions and the selenium coronand<sup>[64]</sup>.

It is known that selenium coronands have the ability to bind metal ions<sup>[7, 13, 64]</sup>. Our experiments have shown that when selenium coronands are attached to the polymeric chain, the coronands have similar characteristics as the individual selenium coronands (e.g. similar UV absorption maxima at  $\lambda_{\max} \approx 240\text{nm}$ ). However, the poly(selenium coronands) have different interaction abilities compared to the individual coronands. Table 2 lists the metal ions examined for interaction with poly8Se2 and poly16Se4. The UV-visible maxima of the interactions are listed in Table 3.

Poly8Se2 can interact with as many as 11 different ions based on UV-vis measurements (see Table 2). However, It is difficult to say that all these interactions can give the corresponding complexes, because the absorption of 8Se2 dication also occurs at 428 nm. The interaction between LiBF<sub>4</sub>, MgSO<sub>4</sub> and poly8Se2 may result in selenium coronand dication formation or coupling products of dications with neutral ligands in the polymer, which yield  $\sigma \rightarrow \sigma^*$  absorptions at ~440 nm. The detailed mechanism of the interaction of these two ions with poly8Se2 requires further study. We believe that the other nine ions can form charge transfer complexes with poly8Se2 [7, 13, 64]. The complexation of poly8Se2 may be enhanced by the ester side chain of the 8Se2 in the polymer. It is known that side groups on 8Se2 can help it to bind metal ions. For example, 8Se2-OH forms a stable "sandwich" complex with Cu<sup>2+</sup> (metal: ligand=1 : 2)[64] because the adjacent OH group can participate in binding. Similarly, interaction of the ester functionally between neighboring selenium coronands in the polymer may help to stabilize the polymer-cation complexes (Fig. 8). This probably is the reason why poly8Se2 can bind to many kinds of metal ions.

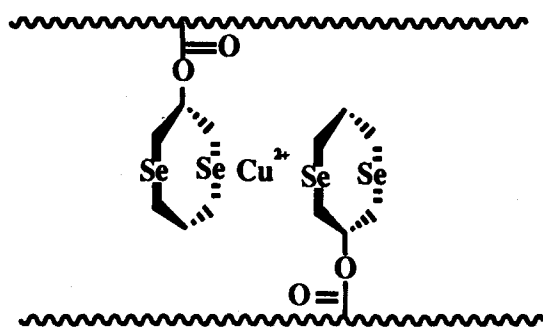


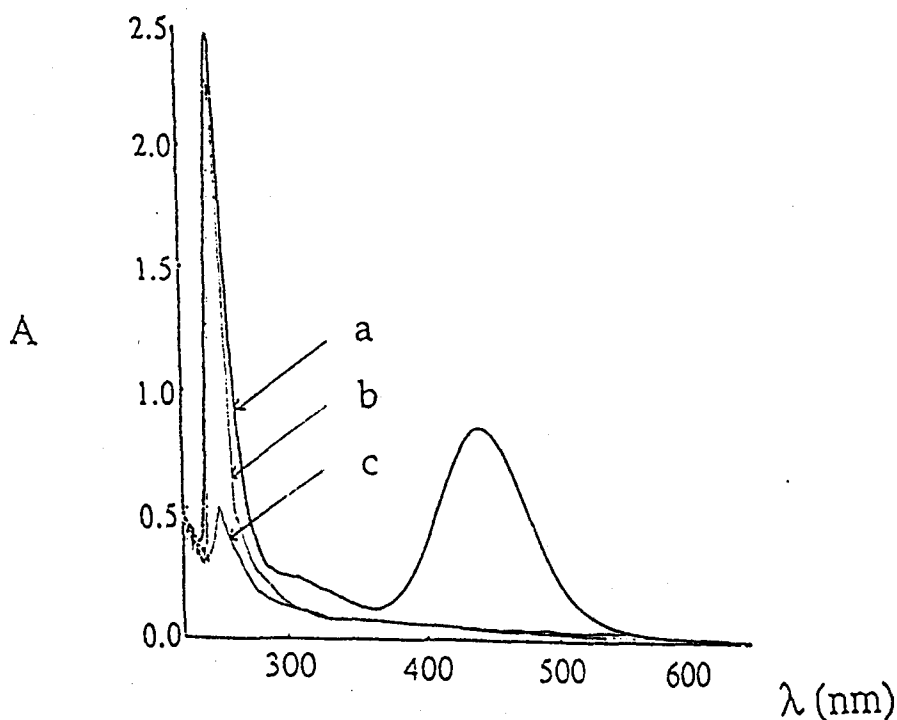
Figure 8. Sandwich structure of Cu(II) polymer complex

For poly16Se4, its complexation is almost the same as the 16Se4 coronand. The side chain shows less of an effect. The size of the large coronand may produce a steric constraint and prevent face-to-face complexation. Poly16Se4 forms complexes with Cu<sup>2+</sup>, Te<sup>4+</sup>, Fe<sup>3+</sup> and Pd<sup>2+</sup> ions only. It therefore seems to have a higher selectivity towards metal ions than poly8Se2.

It is not evident from the data in Table 2 and 3 that the metal ion binding preference of poly8Se2 or poly16Se4 is directly correlated with the hard/soft character of the metal ion. Further detailed kinetic and product studies are necessary before firm conclusions can be drawn.

**Table 2. List of metal ions tested for interaction with poly8Se2 and poly16Se4**

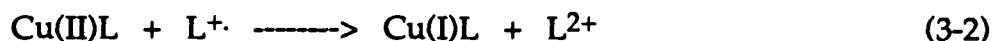
interacting with poly8Se2	Li <sup>+</sup> , Mn <sup>2+</sup> , Fe <sup>3+</sup> , Pd <sup>2+</sup> , Pt <sup>2+</sup> , (Hg <sup>2+</sup> , Hg <sup>+</sup> ), Cu <sup>2+</sup> , Zn <sup>2+</sup> , Sn <sup>2+</sup> Mg <sup>2+</sup> , Te <sup>4+</sup>
Non-interacting with poly8Se2	K <sup>+</sup> , Cs <sup>+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Y <sup>3+</sup> , Eu <sup>3+</sup> , U <sup>4+</sup> , Cr <sup>3+</sup> , Fe <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Ag <sup>+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup> , Al <sup>3+</sup>
interacting with poly16Se4	Cu <sup>2+</sup> , Te <sup>4+</sup> , Fe <sup>3+</sup> , Pd <sup>2+</sup>
Non-interacting with poly16Se4	K <sup>+</sup> , Li <sup>+</sup> , Ag <sup>+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Pt <sup>2+</sup> , Pb <sup>2+</sup> , Mg <sup>2+</sup> , Mn <sup>2+</sup> , (Hg <sup>2+</sup> , Hg <sup>+</sup> ), Zn <sup>2+</sup> , Sn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Cd <sup>2+</sup> , Al <sup>3+</sup> , Y <sup>3+</sup> , Eu <sup>3+</sup> , Cr <sup>3+</sup> , U <sup>4+</sup>



**Figure 9. UV spectra of (a) poly8Se2-Cu<sup>2+</sup> complex, (b) poly8Se2 and (c) Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in CHCl<sub>3</sub> solution.**

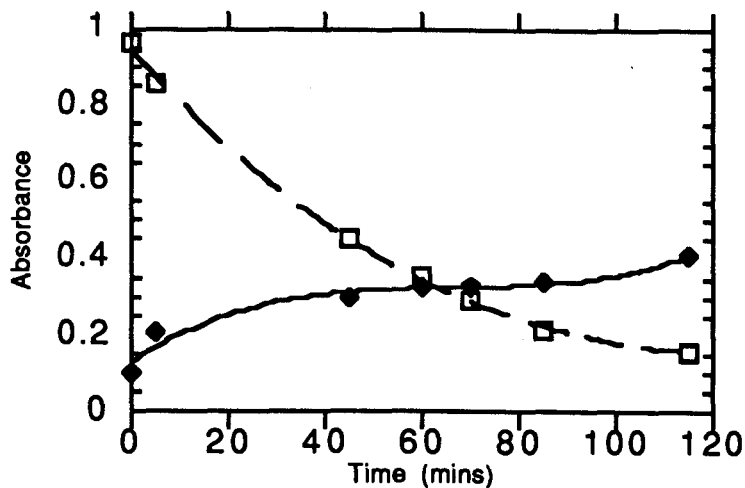
Electron transfer between metal complexes and free crown ligands during the complexation process is an important phenomenon.<sup>[68-71]</sup> The lower the electronegativity of the heteroatoms in the ligands, the higher is the tendency to lose electrons to the metal cations. It was reported<sup>[5, 12]</sup> that selenium coronands such as 16Se4 can undergo a spontaneous electron transfer reaction with its Cu(II) complex in organic solvent to give a Cu(I) complex as well as the intermediate radical cation [16Se4]<sup>+</sup> ( $\lambda_{\text{max}}=318\text{nm}$ ) and the stable dication [16Se4]<sup>2+</sup>(equation 3-1 and 3-2),<sup>[7]</sup>





where L is the coronand ligand and CuL is the complex.

For poly(selenium coronands), we found similar effects. When a certain amount of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  (mole ratio of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  : polymer repeating units = 1 : 30) was added into a poly8Se2/ $\text{CHCl}_3$  solution, the solution turned yellow in less than a second and a strong UV absorption at 440nm appeared(Fig. 9). The solution then decolorized gradually in a few hours and a new peak appeared at  $\lambda_{\text{max}}=327\text{nm}$ . Fig. 10 shows the absorbances at 440 and 327 nm changing with time. After 19 hours, the solution had decolorized (absorbance at 440nm was zero). The new peak at ~327nm is believed to be due to the products of electron transfer between polymer bound coronands and  $\text{Cu}^{2+}$  in the polymer- $\text{Cu}^{2+}$  complex, i.e. the radical cations of selenium coronands produced in this process. We could take this polymer complex out of the solution quickly after the precipitate was formed. By adding more  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  into the polymer solution, more polymer- $\text{Cu}^{2+}$  complex formed and precipitated. The suggestion to take this precipitate out of the solution is based on the supposition that the polymer complex is stable in solid state. The electron transfer processes and subsequent coupling reactions only occurred when the polymer and its complexes were in the non-aqueous solution. Trace water in the solvent can accelerate this process<sup>[64, 67]</sup>. A similar situation was encountered when  $\text{Cu}^{2+}$  ion reacted with poly16Se4 in Chloroform solution. Initially, a peak at 470 nm appeared and decayed with time to give a new absorption band at 328 nm which is assigned to the radical cations by analogy with the work on the monomeric 16Se4 species<sup>[7]</sup>.



**Figure 10** Absorbance changes with time after addition of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  to poly8Se2 ( $\text{CHCl}_3$ ) at room temperature. Solid line: 327nm; dashed line: 440nm

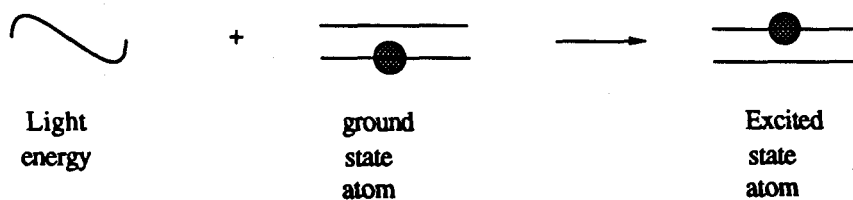
**Table 3.** UV absorption maxima of poly8Se2- and poly16Se4- metal ion solutions <sup>a</sup>

Ions with poly8Se2	$\text{Li}^+$	$\text{Mg}^{2+}$	$\text{Mn}^{2+}$	$\text{Fe}^{3+}$	$\text{Pd}^{2+}$	$\text{Pt}^{2+}$	$\text{Hg}^{2+}$	$\text{Hg}^+$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Sn}^{2+}$	$\text{Te}^{4+}$
$\lambda_{\text{max}}(\text{nm})$	434	444	382	466	380	430	312	288	434	464	444	402
Ions with poly16Se4	$\text{Cu}^{2+}$	$\text{Te}^{4+}$	$\text{Fe}^{3+}$	$\text{Pd}^{2+}$								
$\lambda_{\text{max}}(\text{nm})$	480	390	364	318								

<sup>a</sup> In  $\text{CHCl}_3$

### 3.2.2. Atomic Absorption Spectroscopic Measurements of Polymer-Cu Complexes

Every element has a specific number of electrons associated with its nucleus. The normal and most stable orbital configuration of such an atom is known as the "ground state". The "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state". The amount of light absorbed is proportional to the number of atoms in the light path. By measuring the amount of light absorbed, a quantitative determination of the amount of an analyte can be made. The use of a special light source and careful selection of wavelengths allow the specific determination of individual elements. The process of atomic absorption is illustrated in Fig. 11.



**Figure 11. Atomic absorption process**

In this experiment, the quantity of Cu in the polymer-Cu<sup>2+</sup> complexes was determined as follows: (1) boiling a known amount of the polymer-Cu<sup>2+</sup> complex in concentrated nitric acid for a few hours to free the Cu<sup>2+</sup> ion, (2) dilution of the Cu<sup>2+</sup> nitric acid solution, (3) measurement of the absorbance of this solution by atomic absorption spectroscopy (AAS), (4) comparison of the absorbance with the calibration line of Cu<sup>2+</sup> and determination of the

amount of  $\text{Cu}^{2+}$  in the solution. The calibration data and AAS data of  $\text{Cu}^{2+}$  in the polymer complexes are listed in Table 4 and 5, respectively.

**Table 4. AAS calibration data of  $\text{Cu}^{2+}$  in water**

Concentration (ppm)	1.27	2.54	3.81	5.08	6.35
Absorbance	0.082	0.167	0.245	0.320	0.392

**Table 5. AAS data of  $\text{Cu}^{2+}$  in the polymer complexes**

Sample	Poly8Se2- $\text{Cu}^{2+}$	Poly16Se4- $\text{Cu}^{2+}$
Weight of sample (mg)	2.6	2.1
Absorbance of $\text{Cu}^{2+}$	0.314	0.298
$\text{Cu}^{2+}$ in the sample ( $\mu\text{g}$ )	150.3	141.8
$\text{Cu}^{2+}$ in the sample (% , w/w)	5.78 $\pm$ 0.01	6.75 $\pm$ 0.01
Theoretical amt. of $\text{Cu}^{2+}$ in the sample (% , w/w)*	6.45	6.94

\* Theoretical calculation of  $\text{Cu}^{2+}$  % (w/w) in the sample is based on the ratios of polymer unit to  $\text{Cu}^{2+}$  = 2 : 1 for poly8Se2- $\text{Cu}^{2+}$  complex and 1 : 1 for poly16Se4- $\text{Cu}^{2+}$  complex.

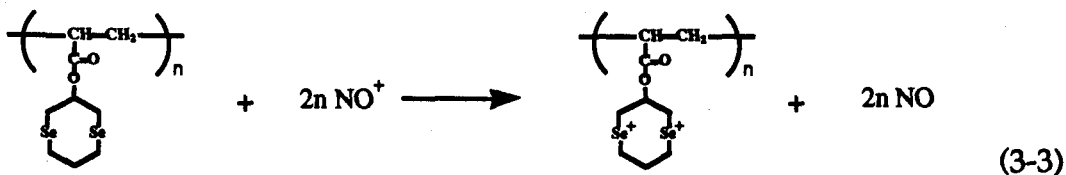
The results showed that poly8Se2- $\text{Cu}^{2+}$  contained 5.78%(w/w) of Cu. The theoretical prediction for a 1 : 2 ratio of  $\text{Cu}^{2+}$  to the poly8Se2 repeating unit is 6.45%. Comparison of the experimental result of  $\text{Cu}^{2+}$  (5.78%) in poly8Se2- $\text{Cu}^{2+}$  and the former structure of  $\text{Cu}(\text{II})(8\text{Se2-OH})_2$  in which the ratio of  $\text{Cu}^{2+}$  to 8Se2 is 1 : 2<sup>[64]</sup> suggests a sandwich structure might be

expected, as in Fig. 8. The procedure was repeated for poly16Se4-Cu<sup>2+</sup> (see Table 5). The results show that the ratio of Cu<sup>2+</sup> to the poly16Se4 repeating unit is 1 : 1 in this poly16Se4-Cu<sup>2+</sup> complex. It is likely that the Cu<sup>2+</sup> ion in the poly16Se4-Cu<sup>2+</sup> complex is inside the 16Se4 ring, similar to the situation with the 16Se4-Cu<sup>2+</sup> complex<sup>[7]</sup>.

### 3.3. Study of the Redox Properties of Polymers and Copolymers

#### 3.3.1. Chemical Oxidation of Polymers

Selenium coronands exhibit a rich redox chemistry<sup>[7, 13]</sup>. Similarly polymers with pendant selenium coronands can be oxidized both chemically and electrochemically. For example, the polymers can be chemically oxidized by NOBF<sub>4</sub> as determined by the change in UV-vis absorption spectrum. Upon addition of poly8Se2 into excess NOBF<sub>4</sub> /dichloromethane, selenium coronand dication is formed (UV absorption at λ<sub>max</sub>=428.8nm). The oxidation reaction is as follows:



The absorption band decreases quickly with time, yielding a colorless solution. This is believed to be due to combination of the cations of selenium coronands. For the reaction of poly16Se4 with NOBF<sub>4</sub>, a peak at λ<sub>max</sub>=326nm, corresponding to the absorption of the dication of 16Se4,<sup>[7]</sup> is observed.

### 3.3.2. Cyclic Voltammetry

#### 3.3.2.1. Technical Background

Cyclic voltammetry (CV) is a relative simple technique capable of providing a great deal of useful information on redox activity<sup>[65]</sup>. In CV, a cyclic or triangular potential-time waveform is used (Fig. 12a). The resulting current, which flows through the cell, is recorded as a function of the potential of the working electrode. In the presence of an electroactive material that undergoes reversible electron transfer, the linear-sweep voltammogram (current-potential curve) normally shows a peak rather than a plateau (Fig. 12b). This characteristic shape may be qualitatively understood as follows: The forward sweep in Fig. 12b refers to an increase in positive potential. The current at first is non-Faradaic, corresponding to the change in the capacity of the electric double layer as the electrode potential is changed. As the potential becomes more positive, the current rises exponentially. However, as current flows, a progressive depletion of material near the electrode surface results. At the peak current  $i_{p_a}$ , the concentration of the reactant at the electrode surface is virtually zero. The potential is called the anodic peak potential  $E_{p_a}$ . The current subsequently decreases until a diffusion-limited condition is obtained as in classical polarography.

As the potential is reversed in a negative direction, the product formed during the forward (anodic) sweep is still in the vicinity of the electrode and may itself be reduced at the electrode surface at sufficiently less positive potential. There is again a rapid increase in current, and at a particular

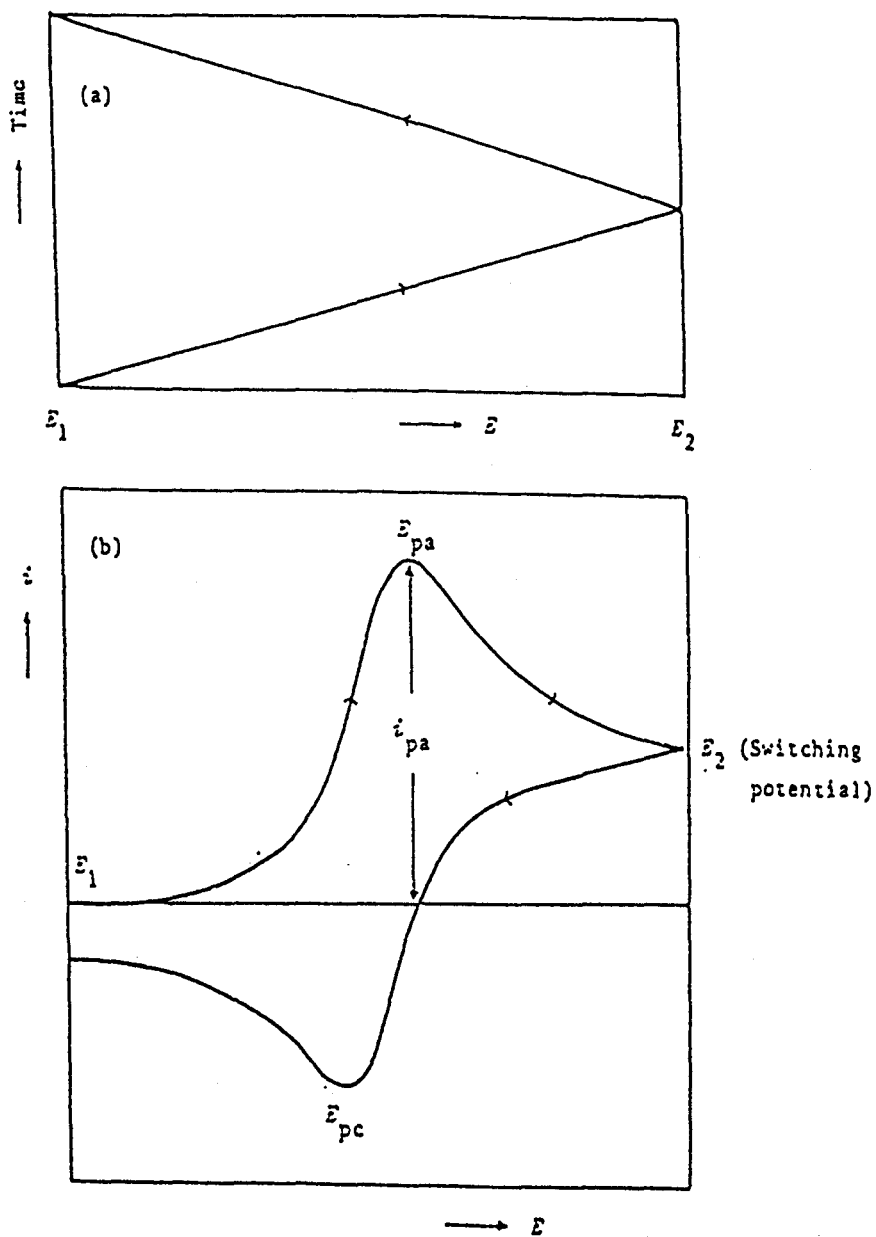


Figure 12. (a) Cyclic potential sweep. (b) Resulting cyclic voltammogram.

potential  $E_{p_c}$ , a maximum cathodic current  $i_{p_c}$  is observed. Beyond this point, the current decreases to a diffusion-limited value. In the multisweep method several consecutive  $i$ - $E$  curves are recorded while the applied potential undergoes its periodic variations with time. Changes in the concentrations of the electroactive species at the electrode surface (and this includes the products of the reaction) from one cycle to another are reflected in the  $i$ - $E$  profiles.

For a simple system, a reversible electron transfer at a planar electrode, the peak current is equal to

$$i_p = 2.687 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad \text{at } 25^\circ\text{C} \quad (3-4)$$

where  $i_p$  is the peak current in microamperes,  $n$  is the number of electrons involved in the oxidation or reduction,  $A$  is the area of the electrode in  $\text{cm}^2$ ,  $D$  is the diffusion coefficient of the electroactive species in  $\text{cm}^2/\text{s}$ ,  $C$  is the concentration of the electroactive species in the solution in  $\text{mmol/l}$ , and  $v$  is the sweep rate in  $\text{V/s}$ . Equation (3-4) predicts that the peak current will be proportional to the square root of the sweep rate for diffusion controlled processes.

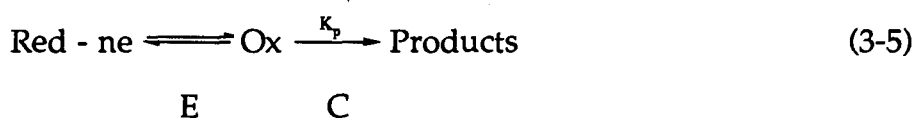
Cyclic voltammetry is a convenient way of testing for electrochemical reversibility. For example, for a reversible (Nernstian) system, where electron-transfer reactions proceed with high heterogeneous rate constants, the ratio of the peak current for the cathodic process relative to the peak current for the anodic process,  $i_{p_a}/i_{p_c}$  is equal to unity. Other reversibility criteria include: separation peak and/or half-peak potentials of  $\Delta E_p = \Delta E_{p/2} =$



57/n mV; the dependency of current on the square root of the sweep rate; and the constant anodic peak potential  $E_{pa}$  or  $i_{pa}/\nu^{1/2}$  with  $\nu$ .

If electron-transfer rates are low on the time scale of the potential sweep, then the Nernstian equilibrium following a change in electrode potential is not achieved relative to the potential sweep rate. The redox reaction is then said to be "irreversible" and the peak potentials are separated by values greater than those for a reversible system ( $> 0.057/n$  mV). In between the "reversible" and "irreversible" regions falls a gray area for which the electrochemical process is termed "quasi-reversible".

Cyclic voltammetry is a good method to study the mechanism of an electrochemical reaction. Especially important in organic electrode reactions are situations in which homogeneous chemical reactions are coupled to the electron transfers. Several possibilities exist. Chemical reactions may follow a reversible electron transfer:

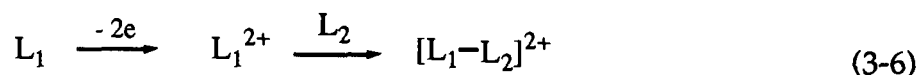


such that a fraction of the oxidized form of the couple reacts chemically and is not available for reduction upon sweep reversal. This type of reaction is called an EC process, indicating that an initial electron transfer is followed by a chemical reaction. In addition, a chemical reaction may be coupled between two successive electron transfers, and this is commonly referred to as an ECE mechanism, and so on. The features characteristic of each can in most cases

be determined by the way the peak currents and potentials vary with sweep rate.

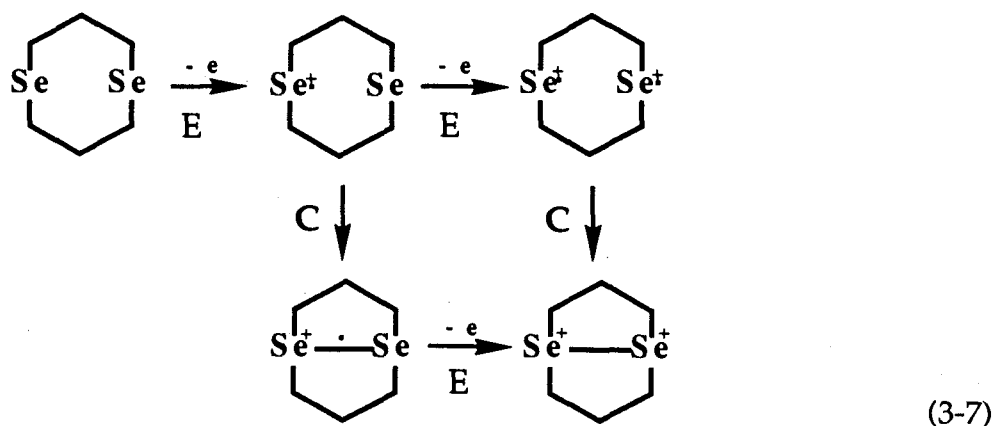
### 3.3.2.2. CV Study of Polymers

Selenium coronands such as 8Se<sub>2</sub> and 16Se<sub>4</sub> can be oxidized at electrodes (see Table 6). The redox processes are complex due to chemical reactions following electron transfer. These chemical reactions may proceed through two paths: intermolecular coupling of oxidized species with neutral ligands, as shown in the following equation:



where L is the selenium coronand and the subscripts indicate different selenium coronands in the redox process; The other pathway involves intramolecular rearrangement such as the transannular stabilization<sup>[5, 12]</sup>. It is both inter- and intra-molecular processes which affect the reversibility of the redox process. Thus, the reversibility of the redox processes of selenium coronands depends both on their relative concentration and structure .

From the cyclic voltammetric study of 8Se<sub>2</sub> and 16Se<sub>4</sub> in acetonitrile, it is found that the redox of 8Se<sub>2</sub> is a quasi-reversible process which involves two electrons<sup>[64]</sup> at a scan rate of 20 mv/s. When the scan rate is increased, two oxidation peaks were observed (Fig. 13). A possible mechanism of this oxidation is as follows:



Following oxidation of 8Se<sub>2</sub> to form a radical cation, either a second electron is removed to form a di-radical cation and subsequently formation of a transannular bond. Alternatively, the radical cation can undergo transannular stabilization prior to losing a second electron. At a fast scan rate two oxidation peaks are observed due to two "one electron transfer" steps. This is an evidence for a "slow" transannular reaction. The oxidation process is designated an EEC (electrochemical-electrochemical-chemical) process. At slow scan rate, e.g., 20 mv/s, transannular stabilization can occur on the time scale of the experiment so that only one oxidation peak is observed. This involves a two electron process.<sup>[64]</sup> This oxidation process is termed an ECE (electrochemical-chemical-electrochemical) process.

From equation 3-6, the opportunity exists for inter-coronand reactions between oxidized coronands and free neutral coronands during the electrochemical process. Thus, the concentration of coronand will play an important role during the electrochemistry. Indeed, as the concentration of

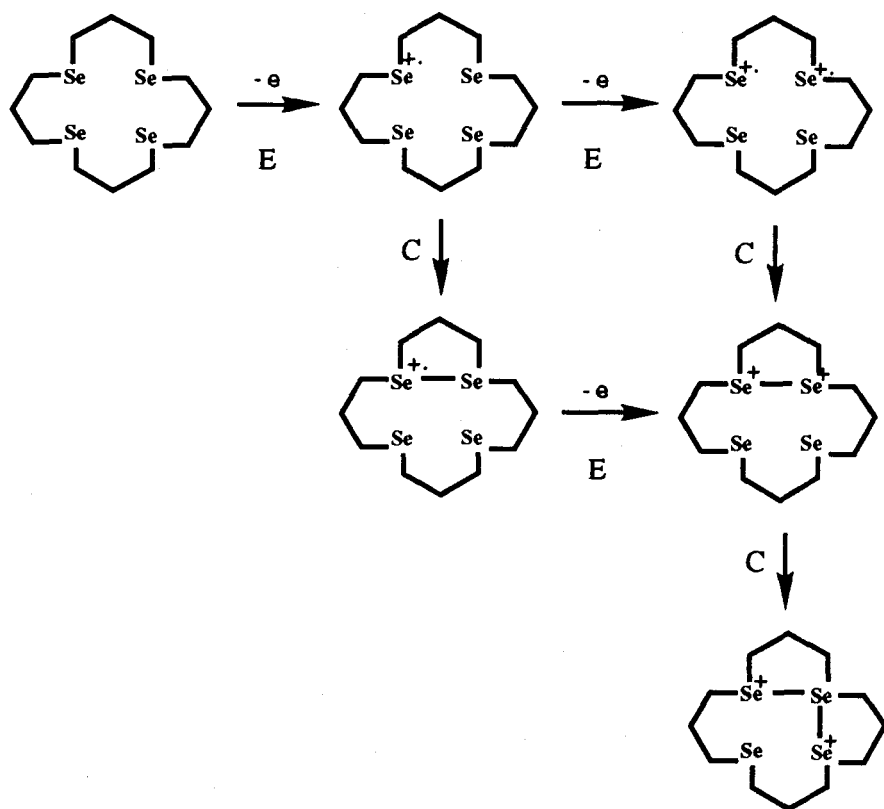
**Table 6. Redox potentials of 8Se2 and 16Se4 on a carbon electrode under different conditions**

(mv)	Sample	Conc. (M)	Oxidation potential (mV)			Reduction potential		
			Peak1	Peak2	Peak 3	Peak1	Peak2	Peak3
8Se2 in CH <sub>2</sub> Cl <sub>2</sub>	1x10 <sup>-4</sup>		450			330		
	1x10 <sup>-3</sup>		550			170		
	1x10 <sup>-2</sup>		820					
8Se2 in CH <sub>3</sub> CN	2x10 <sup>-4</sup>		450	530		370	480	
	2x10 <sup>-3</sup>		460			370		
	2x10 <sup>-2</sup>		550	645	940	380		
8Se2 in (CH <sub>3</sub> ) <sub>2</sub> CO	8x10 <sup>-4</sup>		460	530		370		
16Se4 in CH <sub>2</sub> Cl <sub>2</sub>	3.3x10 <sup>-4</sup>		710	1170	1640	270	-20	-220
	1x10 <sup>-3</sup>		795	893		196		
	1x10 <sup>-2</sup>		1025					
16Se4 in CH <sub>3</sub> CN	1x10 <sup>-4</sup>		555	1100		370		
	1x10 <sup>-3</sup>		633	1210		350		
	1x10 <sup>-2</sup>		772	1410		400	1245	
16Se4 in (CH <sub>3</sub> ) <sub>2</sub> CO	1x10 <sup>-3</sup>		730	1250		800	380	

\* The above potentials were recorded at a scan rate of 20 mV/sec., vs an Ag/AgCl reference electrode.

the selenium coronand is increased, the chance of intermolecular reaction of the oxidized products increases, and it becomes more difficult to observe the corresponding reduction peak. This can be seen from Fig. 14. The cyclic voltammograms show that the redox process of 8Se2 becomes increasingly irreversible when the concentration was raised from  $10^{-3}$  M to  $10^{-2}$  M. In addition, a red/brown precipitate formed near the electrode surface during the oxidation process of 8Se2 at the concentration of  $10^{-2}$  M when high positive potentials were applied. We believe this is due to the tendency of oxidized forms of 8Se2 to undergo intermolecular reaction; the red/brown precipitate being elemental selenium.

A CV study shows that the redox chemistry of 16Se4 is slightly different to that of 8Se2 (Fig. 15). Each oxidation peak corresponds to a "one electron transfer".<sup>[64]</sup>  $[16Se4]^+$  rapidly forms a transannular bond and the removal of a second electron prior to transannular stabilization (the EE process) is not possible on the time scale of the experiment. It appears oxidation of 16Se4 is dominated by a ECEC process as shown in equation 3-8. Thus, varying the scan rate effects the shapes of cyclic voltammograms to a lesser degree than 8Se2. If the redox process had gone through the EECC as shown in in equation 3-8, then the voltammograms would exhibit considerable scan rate dependence. Similar to 8Se2, the concentration has a great effect on the redox processes of 16Se4 as shown in Fig. 15. However, this effect seems less for 16Se4 presumably because of the relative stability of  $[16Se4]^{2+}$  over  $[8Se]^{2+}$ .



The cyclic voltammetric studies of the monomers (structures 6 and 7 on page 23 and 24) indicate their redox behavior is similar to the corresponding selenium coronands. The double bond associated with the monomer has no obvious effect on the redox properties of the coronand. We have synthesized 1,5,9,13-tetraselenacyclohexadecyl propionate, a compound analogous to mono16Se4 in which the double bond is saturated. The cyclic voltammograms of this compound were similar to that of mono16Se4. The relationship  $i_{pa} \sim v^{1/2}$  of the monomers is shown in Fig. 16. It can be seen from the figure that the oxidations of monomers are diffusion controlled.

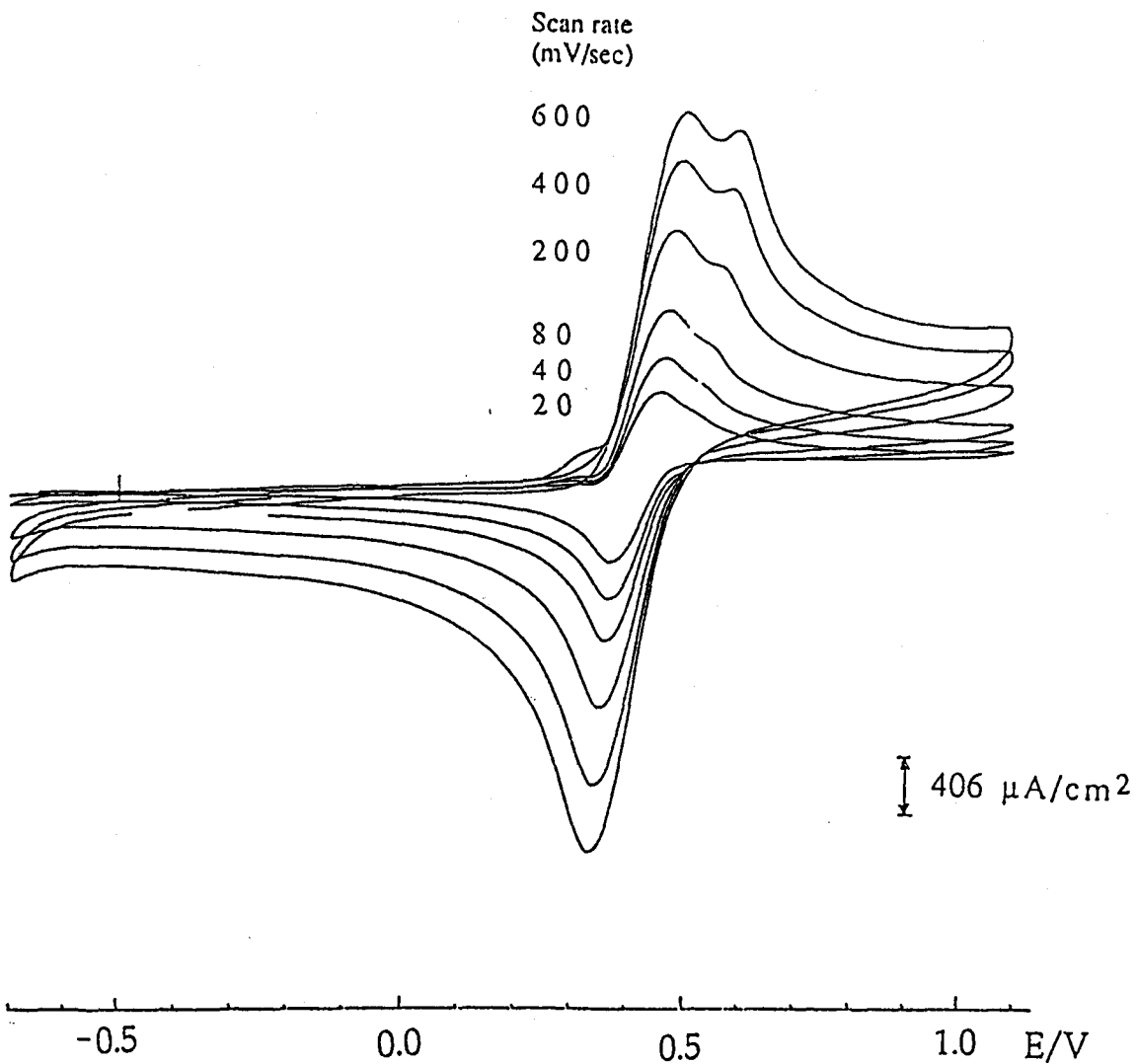


Figure 13. Cyclic voltammograms of  $1 \times 10^{-3}$  M  $8\text{Se}_2$  in acetonitrile at different scan rates. Electrolyte: 0.1 M TEAP/ $\text{CH}_3\text{CN}$ ; electrode: glassy carbon.

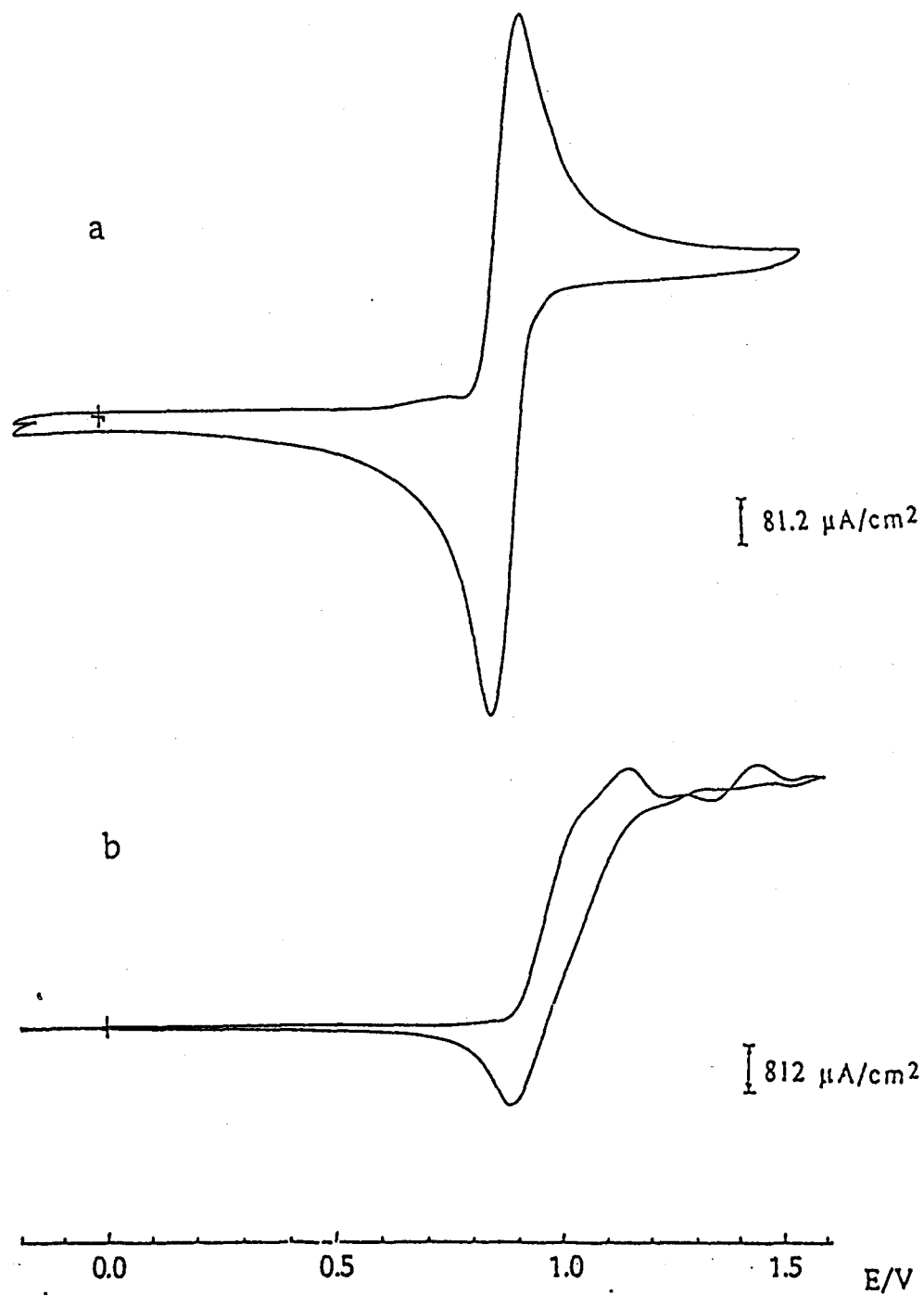


Figure 14. Cyclic voltammetry of 8Se<sub>2</sub> in acetonitrile. (a)  $1 \times 10^{-3} \text{ M}$ , (b)  $1 \times 10^{-2} \text{ M}$ , Electrolyte: 0.1 M TEAP/CH<sub>3</sub>CN; electrode: glassy carbon; scan rate: 20 mV/s.



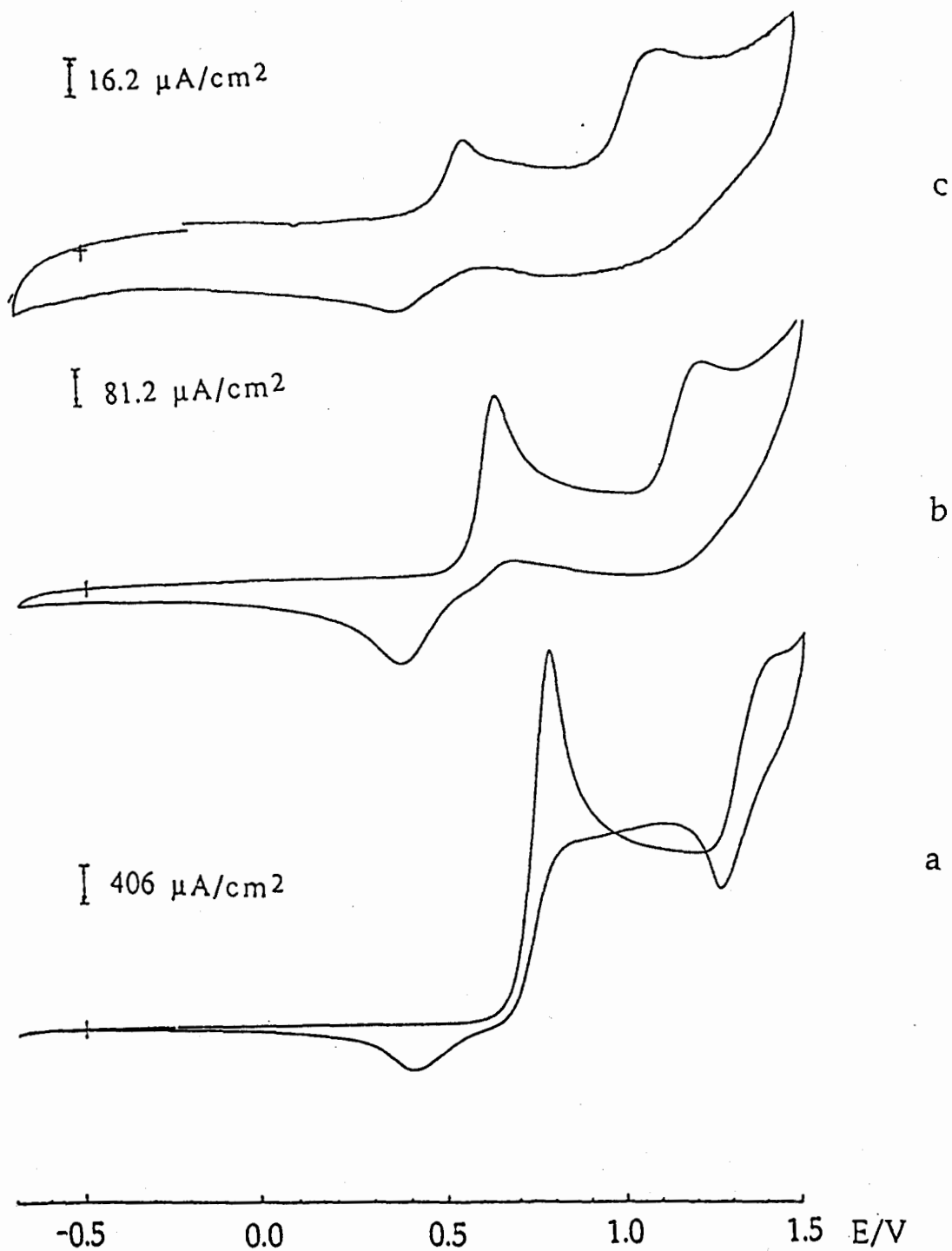
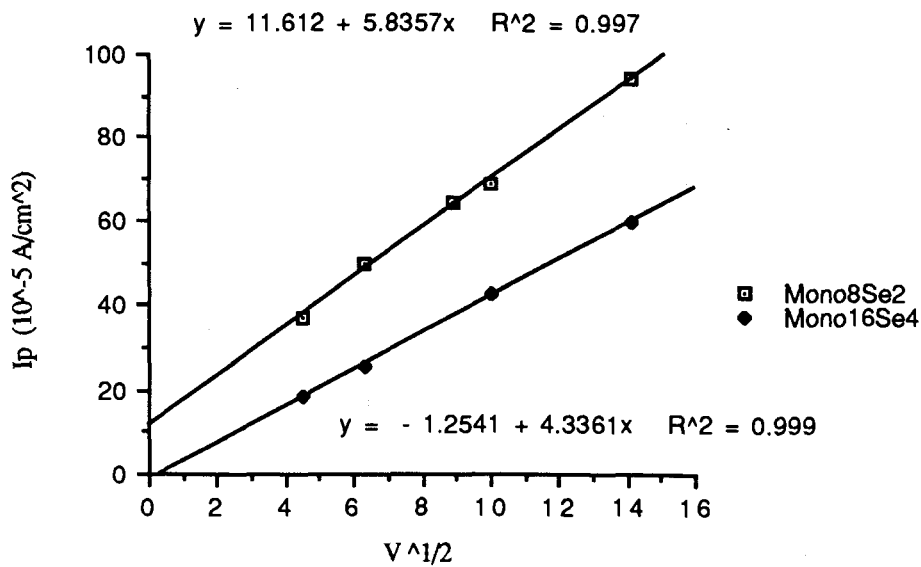


Figure 15. Cyclic voltammograms of 16Se4 in acetonitrile. (a)  $1 \times 10^{-2} M$ , (b)  $1 \times 10^{-3} M$ , (c)  $1 \times 10^{-4} M$ . Electrolyte: 0.1 M TEAP/ $CH_3CN$ ; electrode: glassy carbon; scan rate: 20 mv/s.



**Figure 16. Correlation between oxidation peak current [ $I_p$ ; ( $\text{A}/\text{cm}^2$ )] of mono8Se2,  $2.0 \times 10^{-2} \text{ M}$ ; and mono16Se4,  $1.3 \times 10^{-2} \text{ M}$  and the square root of scan rate.**

In poly(selenium coronands) the coronands are sterically crowded by virtue of their covalent attachment to the polymer backbone. As a result, even through the polymer concentration may be low, the microscopic concentration of selenium coronands is relatively high. In principle the high concentration of coronands might facilitate intermolecular reactions and therefore, the redox properties of the polymer in the solution might be expected to be irreversible. Figures 17 and 18 show cyclic voltammograms of these polymers. Low concentration ( $10^{-3} \text{ M}$ ) show a relatively high degree of reversibility. This is surprising since the local concentration can be calculated to be  $>0.5 \text{ M}$ . The concentration effects reveal some mechanistic aspects of the redox processes. By increasing the concentration of poly8Se2, the reduction peaks gradually disappear because of the increase of the coupling reactions

between oxidized and neutral selenium coronands on different polymer chains. New oxidation peaks appear at higher concentration due to the subsequent oxidation of the products of intermolecular reactions.

**Table 7. Redox potentials of the monomers, polymers and co-polymers vs Ag/AgCl at a scan rate of 20 mv/s.**

Sample	Solution	Oxidation potential		Reduction potential	
		Peak 1	Peak 2	Peak 1	Peak 2
Mono8Se2 <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	875mv		405mv	
Mono16Se4 <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	1080mv	1450mv		
Poly8Se2 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	410mv	950mv	400mv	
Poly16Se4 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	580mv		340mv	-370mv
CoP8Se2-A <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	420mv	1270mv	230mv	80mv
CoP8Se2-B <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> /TEAP	410mv	1280mv	295mv	
Poly8Se2 <sup>*</sup>	CH <sub>3</sub> CN/TEAP	530mv		390mv	
Poly16Se4 <sup>*</sup>	CH <sub>3</sub> CN/TEAP	700mv		240mv	

<sup>a</sup> monomers in  $1 \times 10^{-2}$  M

<sup>b</sup> polymers and copolymers in  $1 \times 10^{-3}$  M

<sup>\*</sup> Polymer coated electrode

For poly16Se4, no obvious changes in the shapes of voltammograms with increasing concentration are observed (Fig. 17). However, the constant peak current implies electroprecipitation which will interfere with inter-selenium coronand reactions. In essence, electroprecipitation forms a polymer modified electrode. It will be shown in a following section that

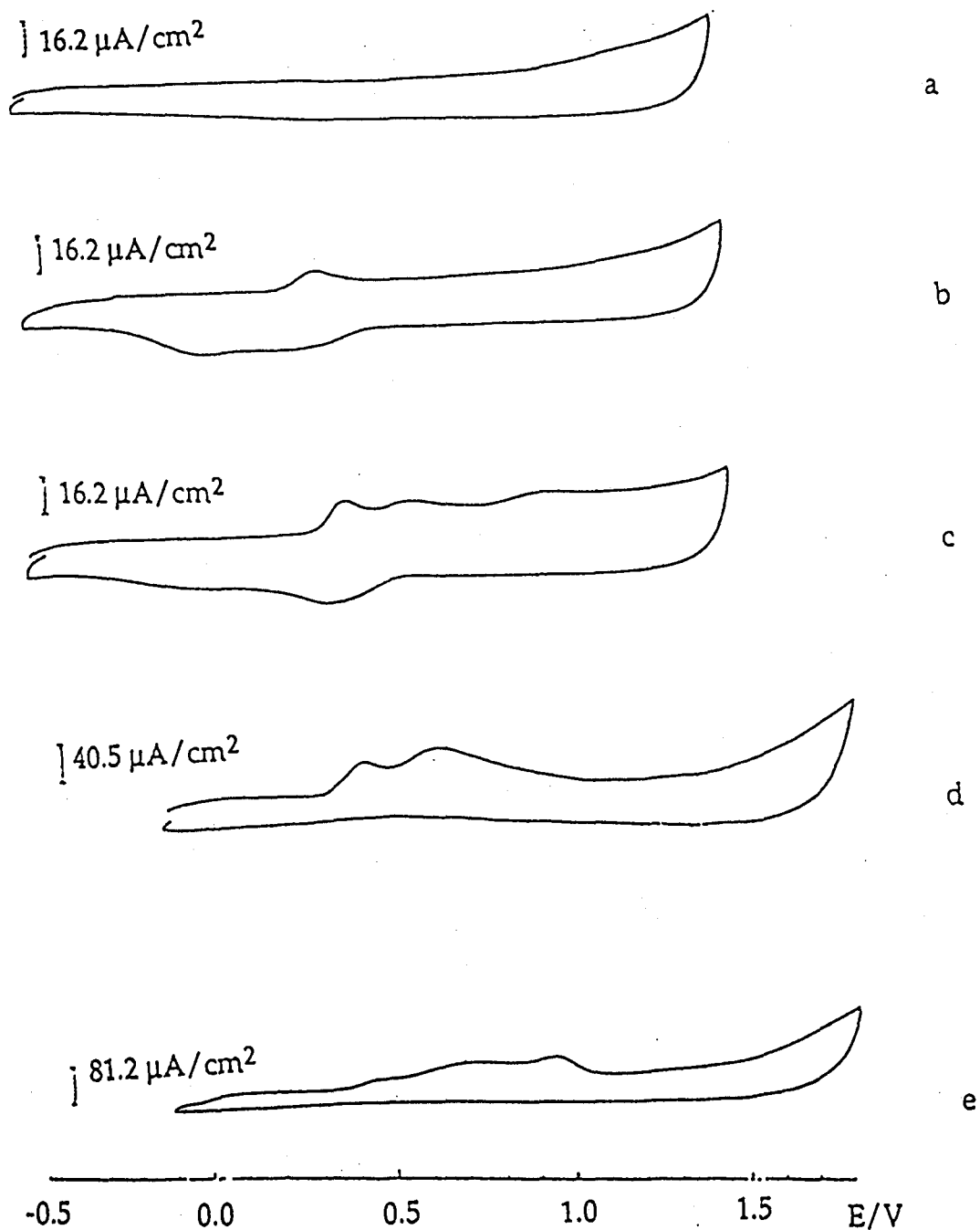


Figure 17. Cyclic voltammetry of poly8Se2 in dichloromethane. (a)  $1 \times 10^{-5}$  M, (b)  $1 \times 10^{-4}$  M, (c)  $1 \times 10^{-3}$  M, (d)  $1.3 \times 10^{-2}$  M, (e)  $3.2 \times 10^{-2}$  M. Electrolyte: 0.1 M TEAP/ $\text{CH}_2\text{Cl}_2$ ; electrode: glassy carbon; scan rate: 20 mv/s. Concentrations are with respect to pendant selenium coronands.

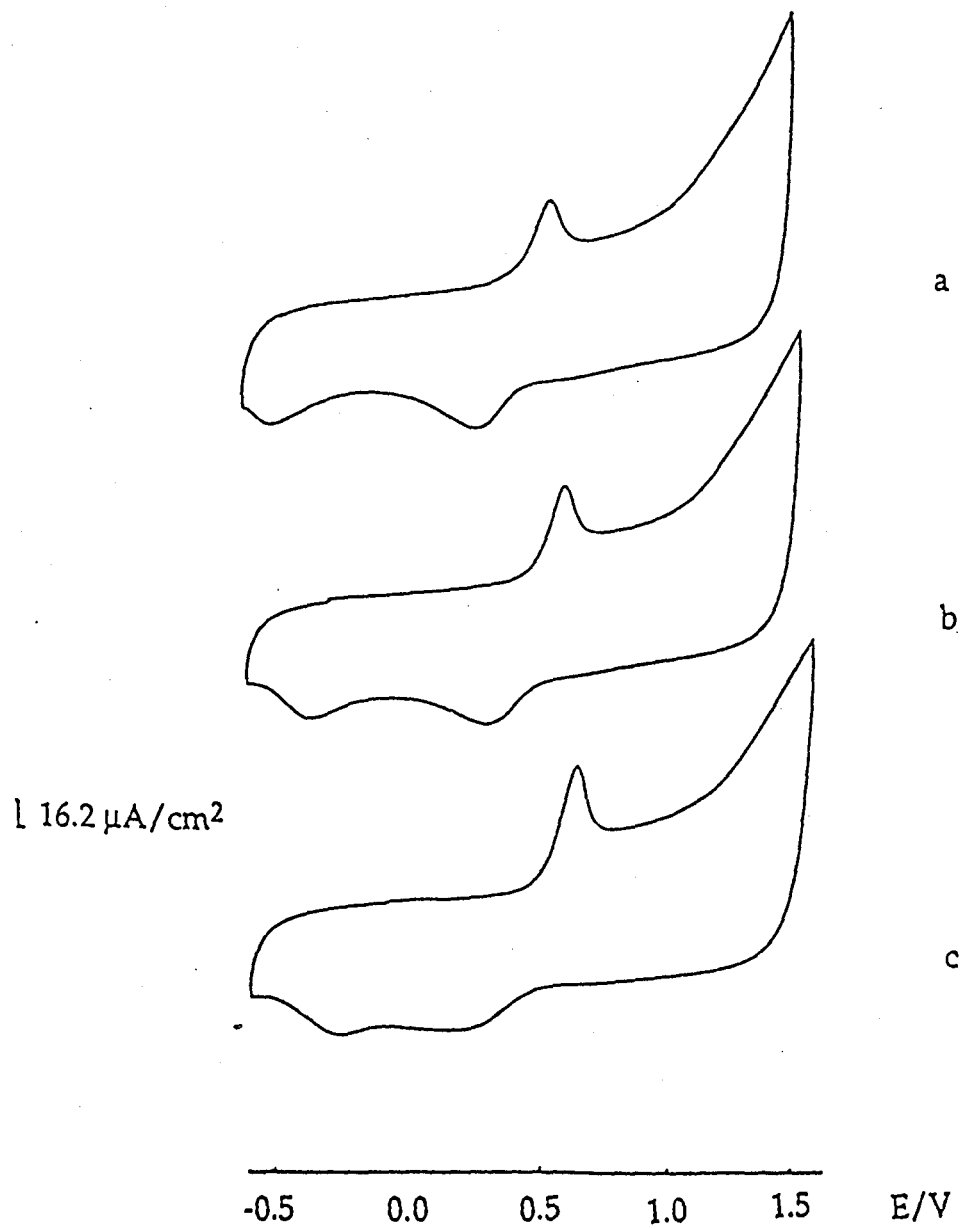


Figure 18. Cyclic voltammetry of poly16Se4 in dichloromethane. (a)  $1 \times 10^{-4}$  M, (b)  $1 \times 10^{-3}$  M, (c)  $5 \times 10^{-3}$  M. Electrolyte: 0.1 M TEAP/ $\text{CH}_2\text{Cl}_2$ ; electrode: glassy carbon; scan rate: 80 mv/s. Concentrations are with respect to pendant selenium coronands.

poly(selenium coronands) in the form of thin films on electrodes exhibits enhanced reversibility/stability over the oxidized polymers in solution.

For copolymers of mono8Se2 / methyl acrylate (CoP8Se2-A, CoP8Se2-B), the diluting effect of methyl acrylate group partially separates selenium coronands (8Se2) on the polymer chains and interrupts electron transfer processes between adjacent selenium coronands. It is this separation effect that provides a partially reversible voltammetry for these copolymers (Fig. 19). Copolymers also show a concentration effect, similar to that of poly8Se2, when the concentration is increased from  $10^{-4}$  to  $10^{-2}$  M.

In the previous section the cyclic voltammetric results for the polymers in solution have been described. However, for applications of ion-selective or ion permeable membranes, it is necessary to study redox process in swollen films. This was achieved by using polymer modified electrodes. Cyclic voltammograms of polymer modified electrodes (polymer coated onto the surface of the electrode) have been studied (Fig. 20). For poly8Se2, the redox couple is partially reversible. This is remarkable given that the concentration of 8Se2 in the film is calculated to be  $< 3$  M. We believe this is due to physical constraint of the selenium coronands in the film which diminishes irreversible coupling reactions of the coronands. Polymer modified electrodes using poly16Se4 also exhibited quasi-reversible cyclic voltammograms (Fig. 20b). Again this is a interesting result given the high concentration of poly16Se4.

For Cop8Se2-A and B, the 8Se2 coronands have been diluted (separated) by inert spacers. With this spatial separation, less inter-molecular coupling is

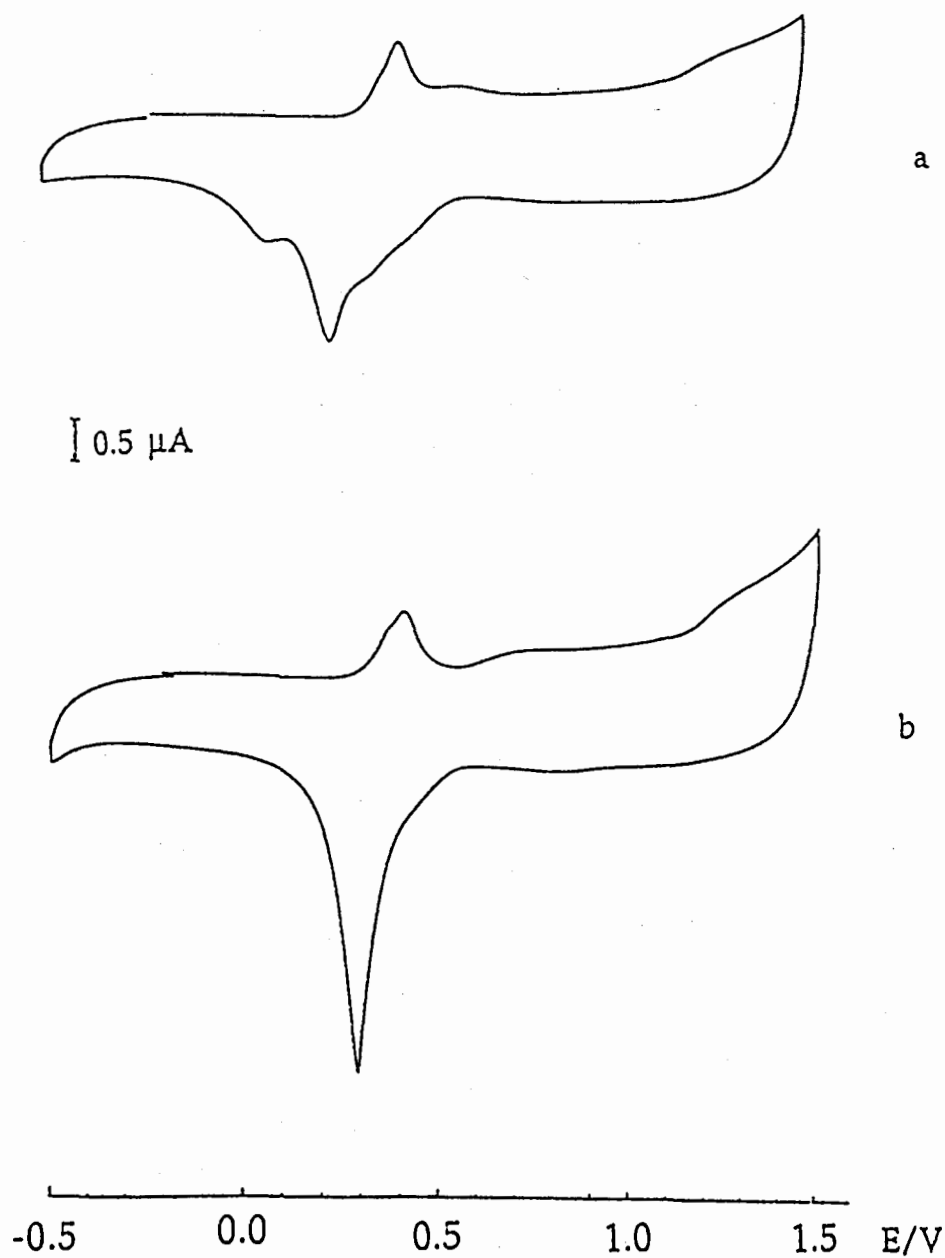


Figure 19. Cyclic voltammetry of copolymers in dichloromethane. (a) cop8Se2-A,  $1 \times 10^{-3}$  M, (b) cop8Se2-B,  $1.05 \times 10^{-3}$  M. Electrolyte: 0.1 M TEAP/ $CH_2Cl_2$ ; electrode: glassy carbon; electrode area:  $0.057 \text{ cm}^2$ ; scan rate: 20 mv/s. Concentrations are with respect to pendant selenium coronands.

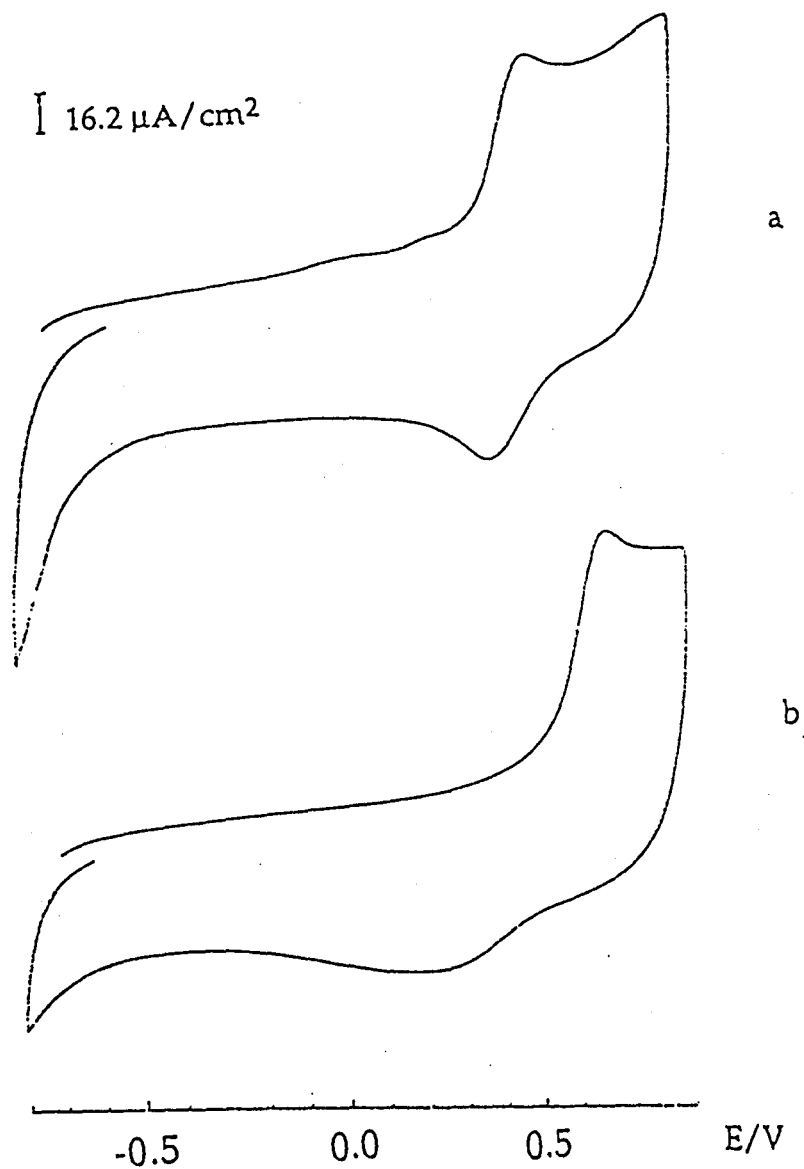
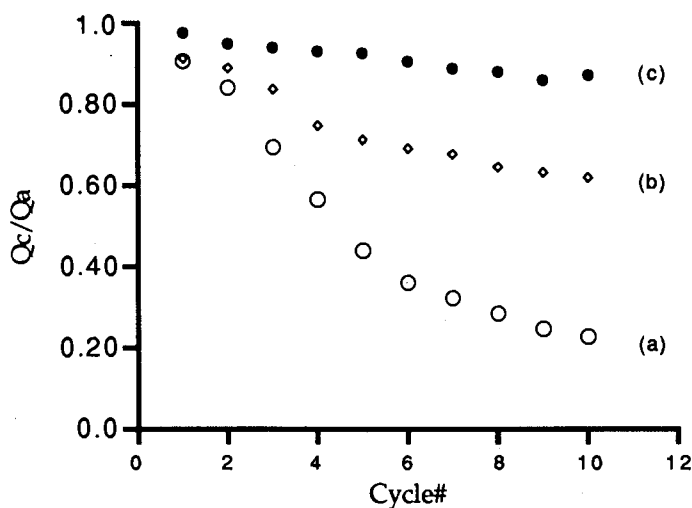


Figure 20. Cyclic voltammograms of carbon electrodes coated with polymers in acetone. (a) poly8Se<sub>2</sub>, (b) poly16Se<sub>4</sub>. Electrolyte: 0.1 M TEAP/CH<sub>3</sub>CN; electrode: glassy carbon; electrode area: 0.057 cm<sup>2</sup>; scan rate: 160 mv/s. [Film thickness: (a) 0.1 μm, (b) 1.0 μm].

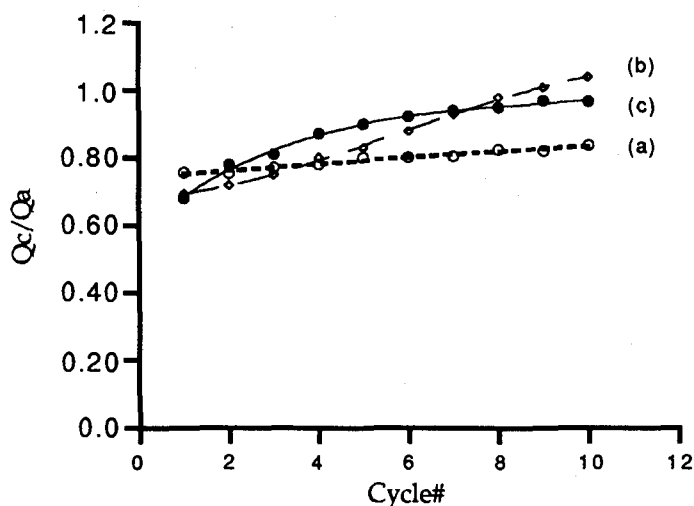


expected and hence more stable and reversible voltammetry is anticipated. The CV studies of modified carbon electrodes indicate redox reversibility increases in the order poly8Se2 < Cop8Se2-A < Cop8Se2-B. This is consistent with the decreasing concentration of 8Se2 in the polymer films. Fig. 21 is used to explain this. Here,  $Q_c$  is the amount of charge (coulombs) under the reduction peaks, and  $Q_a$  is the amount of charge under the oxidation peaks. If the ratio  $Q_c/Q_a$  decreases with number of scans then this indicates irreversibility of the redox process. The copolymers exhibit greater reversibility than poly8Se2 as indicated from  $Q_c/Q_a$  over the first ten cycles (Fig. 21).



**Figure 21**  $Q_c/Q_a$  of the first ten cyclic voltammograms of carbon electrode modified by films of (a) poly8Se2, (b) Cop8Se2-A, (c) Cop8Se2-B in 0.1 M TEAP/CH<sub>3</sub>CN

In complementary experiments, chains of poly(8Se2) were physically separated from one another by preparing blends in which poly8Se2, Cop8Se2-A and Cop8Se2-B were mixed with an inert polymer, poly(methyl acrylate) (PMA). Blends of poly8Se2 with PMA represent polymer systems in which the coronands are adjacent (in close proximity) with one another along the polymer chain but for which the individual chains are diluted in the solid state by inert polymer chains. For blends of Cop8Se2-A and B the coronands are separated to degree along the chain in addition to having the selenium carrying chains diluted. Cyclic voltammetry of the polymer blend modified electrodes give good reversibility as expected (Fig. 22).



**Figure 22**  $Q_c/Q_a$  of the first ten cyclic voltammograms of carbon electrodes modified by films of (a) 1:1 poly8Se2 / poly(methyl acrylate) blend; (b) 1:1 Cop8Se2-A / poly(methyl acrylate) blend; (c) 1:1 Cop8Se2-B / poly(methyl acrylate) in 0.1 M TEAP/CH<sub>3</sub>CN

It was necessary to evaluate the extent of oxidation in the films of polymer modified electrodes in order to determine whether redox activity remained close to the electrode surface (i.e. a monolayer) or propagated throughout the films. The number of moles of coronands involved in oxidation processes can be calculated by the formula:

$$i t = Q = nFN \quad (3-9)$$

where  $i$  is the current (A),  $Q$  is the amount of charge passed (C),  $n$  is number of electrons involved in the redox process,  $F$  is Faraday's constant which equal to 96487 C/mol, and  $N$  is the number of moles of the compound being oxidized [65, 66]. The results are summarized in Table 8. Here  $\Gamma_{\text{exp}}$  is the experimentally observed number of moles of coronand on the electrode surface,  $d$  is the thickness of film coated on the electrode,  $\Gamma_{\text{calc}}$  is the calculation of total moles of coronand in the film. Values of  $\Gamma_{\text{exp}} \sim 10^{-10}$  are typical of monolayer coverages. Thus, it can be seen that oxidation of polymer films occurred only in a few layers close to the electrode surface.

**Table 8. Characteristics of polymer modified electrodes**

item	poly8Se2	poly16Se4
Q (C)	$4.8 \times 10^{-6}$	$4.47 \times 10^{-6}$
$\Gamma_{\text{exp}}$ (Moles oxidized, mol/cm <sup>2</sup> )	$4.35 \times 10^{-10}$	$4.05 \times 10^{-10}$
T (thickness, $\mu\text{m}$ )	0.1	1.0
$\Gamma_{\text{calc}}$ (mol/cm <sup>2</sup> )	$4.54 \times 10^{-8}$	$2.60 \times 10^{-7}$
$\Gamma_{\text{exp}} / \Gamma_{\text{calc}}$	$9.58 \times 10^{-3}$	$1.56 \times 10^{-3}$

It was also found that the nature of the electrolyte dramatically affects the cyclic voltammetry. The oxidation of  $16\text{Se}_4$  in acetonitrile, acetone and dichloromethane is shown in Fig. 23. The differences in the voltammograms is believed due to differences in the polarity and dielectric constant of the solvents. The solvent polarity of acetonitrile and acetone is much larger than that of dichloromethane, so that oxidized species,  $16\text{Se}_4^+$  and  $16\text{Se}_4^{2+}$ , are solvated to a larger degree, thereby reducing irreversible intermolecular coupling reactions.

Another interesting phenomenon observed for these polymers is their poor redox activity on Pt electrodes. The reasons for this may be due to strong surface interactions between the electrode and the selenium coronand<sup>[72-74]</sup>. With the Pt electrode, the selenium in the coronand can in fact adsorb to the Pt surface. This was evident from observing the electrode surface after immersion into the polymer solution (prior to voltammetry) where upon a layer of polymer had adsorbed onto the surface.

In summary, selenium coronands are very electroactive species. Their redox chemistry is complicated due to inter- and intra-molecular reactions which occur following oxidation. In poly(selenium coronands) the coronands are sterically crowded and although the microscopic concentration of selenium coronands is relatively high, intermolecular reactions are prevented to a degree compared to free coronands in solution. This is even more prevalent for polymer films on electrodes where the coronands are even less mobile. The coronands attached to the polymers can also be separated by inert groups by virtue of copolymerization or by blending with

inert polymers. In both cases, the redox reversibility of the selenium coronands are enhanced.

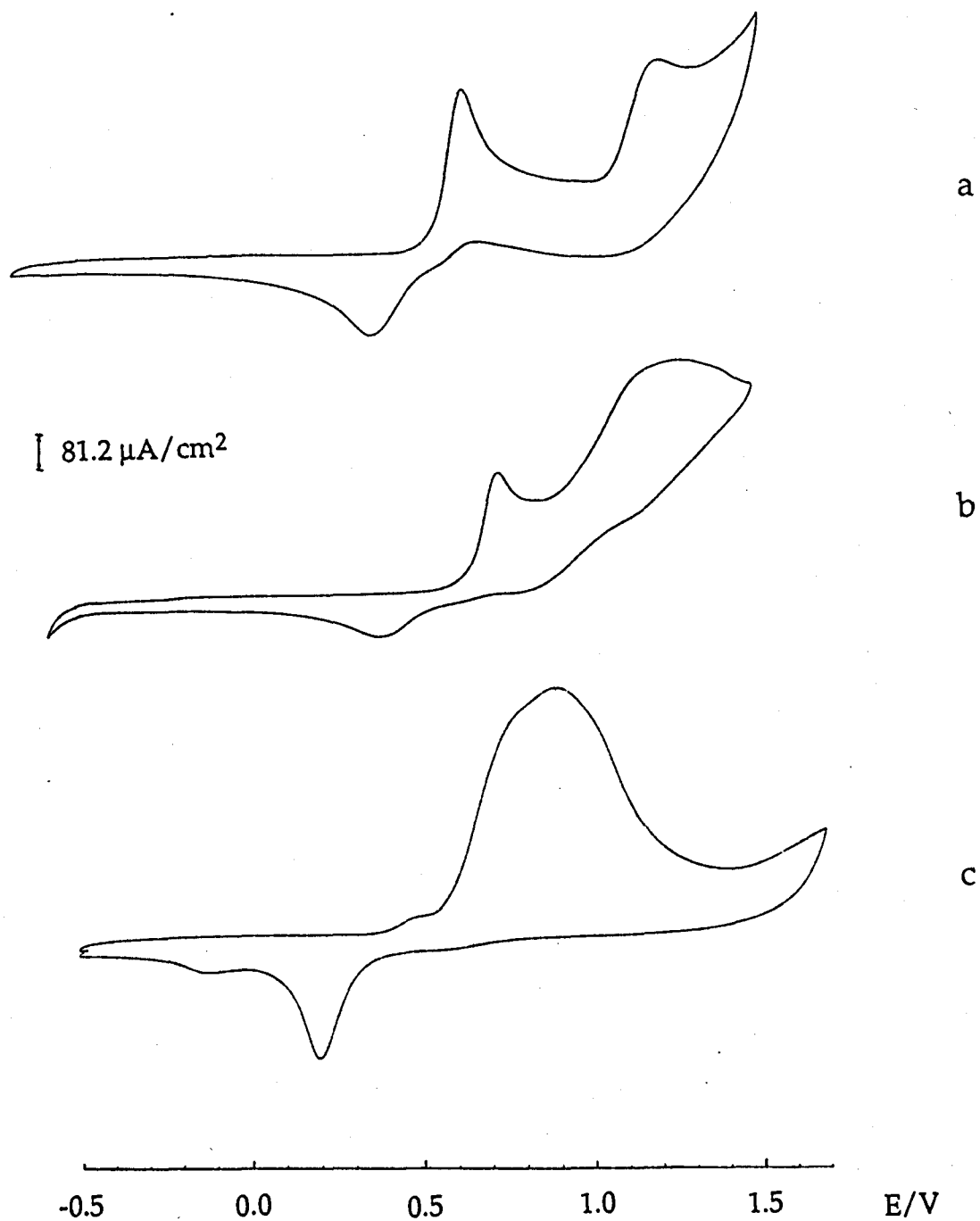


Figure 23. Cyclic voltammograms of  $1 \times 10^{-3}$  M  $16\text{Se}_4$  in different solvents. (a) acetonitrile, (b) acetone, (c) dichloromethane. Electrolyte: TEAP; electrode: glassy carbon; scan rate: 20 mv/s.

## **3.4. Experimental**

### **3.4.1. Measurement of Molecular Weight by GPC**

Poly8Se2 (5 mg) was dissolved in 0.1 ml CH<sub>2</sub>Cl<sub>2</sub> and the solution was diluted to 1 ml with THF. This solution was filtered. The solution (5 μL) was injected into the GPC system fitted with a Spectra-Physics Model SP8000 UV-vis spectrophotometer and a Waters Model R400 refractive index detector. The eluant was THF with a 1 ml/min flow rate. The wavelength 234 nm was selected to measure the UV absorption of the molecule as it eluted.

### **3.4.2. DSC Experiments of Polymers**

Weighed samples in a range of 1.1 ~ 4.9 mg were put into a aluminum cell and squeezed to a tablet. The temperature was raised at a rate of 20 °C/min. between the limits 25 °C and 270 °C. DSC measurements were performed on a Perkin-Elmer DSC-7/TAC-7 instrument.

### **3.4.3. Interaction of Polymers with Metal Ions**

Weighed amounts of the polymer (3.3mg) and metal salts 0.7mg (F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub>Cu were separately dissolved in 2 ml of dry chloroform and 0.2 ml acetone, respectively. The two solutions were mixed in appropriate proportions to obtain polymer-salt complex precipitates. The precipitates were washed with acetone and dichloromethane several times and dried under vacuum. Yield ~100% based on the polymer. The metal salts used

were  $\text{LiBF}_4$ ,  $\text{NaCl}$ ,  $\text{KI}$ ,  $\text{CsNO}_3$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{CoCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{MnI}_2$ ,  $\text{HgNO}_3$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ ,  $\text{AgCF}_3\text{SO}_3$ ,  $\text{Ni}(\text{CF}_3\text{COO})_2$ ,  $\text{SnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{PtCl}_2$ ,  $\text{PdCl}_2$ ,  $\text{YCl}_3$ ,  $\text{EuCl}_3$ ,  $\text{ThF}_4$ ,  $\text{TeCl}_4$ ,  $\text{UF}_4$ .

### 3.4.4. Atomic Absorption Spectroscopy

Weighed amounts of polymer- $\text{Cu}^{2+}$  complexes (2.2 ~ 3.0 mg) were added to 5 ml of concentrated nitric acid. The mixtures were boiled for 3 ~ 4 hrs until about 1 ml of solution remained. The residues were diluted to 30ml with distilled water. The absorbance (A) of  $\text{Cu}^{2+}$  ions in this solution was measured through a double beam Perkin-Elmer 1100B Atomic Absorption Spectrophotometer (Fig. 24). The corresponding concentration of  $\text{Cu}^{2+}$  was determined from a calibration curve.

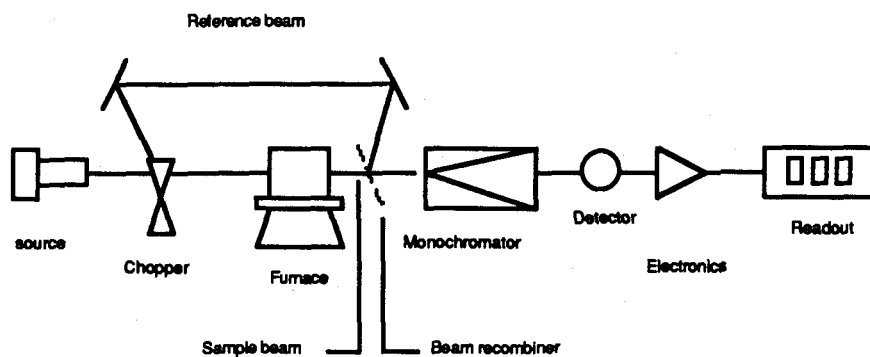


Figure 24. Double-beam atomic absorption spectrophotometer



### 3.4.5. Chemical Oxidation of Polymers

Under an  $N_2$  atmosphere,  $NOBF_4$  (8 mg) was placed in an UV cell. The cell was sealed by a rubber stopper. 1 ml of dried  $CH_2Cl_2$  was syringed into the UV cell to dissolve the  $NOBF_4$ , followed by 3 ml of polymer (10 mg)/ $CH_2Cl_2$  was added into the cell and an in-situ UV-visible measurement was made.

### 3.4.6. Cyclic Voltammetric Measurements

A three-electrode system was used for cyclic voltammetry (see Fig. 25). The cell had provisions for a working electrode (WE), a counter electrode (CE), a reference electrode (RE), inert-gas purge, and maintenance at a constant temperature ( $25^\circ C$ ). It was desirable to minimize solution resistance by using a supporting electrolyte concentrations of 0.1 M in solvents such as

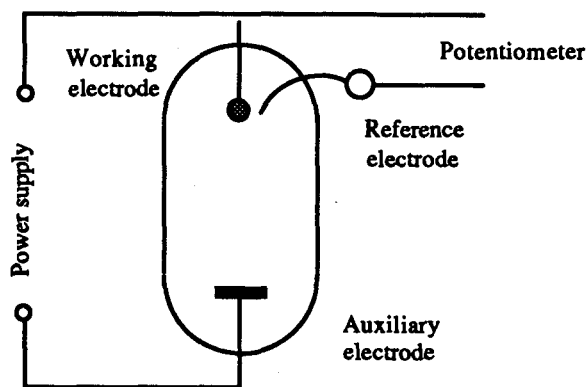


Figure 25. Three-electrode cell system

acetonitrile, dichloromethane, DMF, and methanol. Dichloromethane, acetonitrile and acetone were chosen as the solvents according to the

solubility of the products in them. The potentials reported are based on KCl(saturated)-Ag/AgCl. The supporting electrolyte used for these studies was TEAP (tetraethylammonium perchlorate). The solutions were flushed with N<sub>2</sub> for about 10 mins prior to use.

The working electrodes (WE) were C or Pt disc electrodes, which were polished with 3 μm aluminum oxide powder (Micro Metallurgical Ltd.), and washed with distilled water and acetone several times before each experiment. The counter-electrode (CE) was a Pt wire and reference electrode (RE) was KCl(saturated)-Ag/AgCl<sup>[75]</sup>. The potential range was -1.2 ~ +1.6 V for TEAP (tetraethylammonium perchlorate)/CH<sub>2</sub>Cl<sub>2</sub>. All potentials are reported with respect to Ag/AgCl. The sweep rate was varied between 20 ~ 200 mV sec<sup>-1</sup>. Electrochemical studies were performed on a Pine RDE4 bipotentiostat and a Hewlett-Packard HP 7046A X-Y recorder.

# Chapter 4

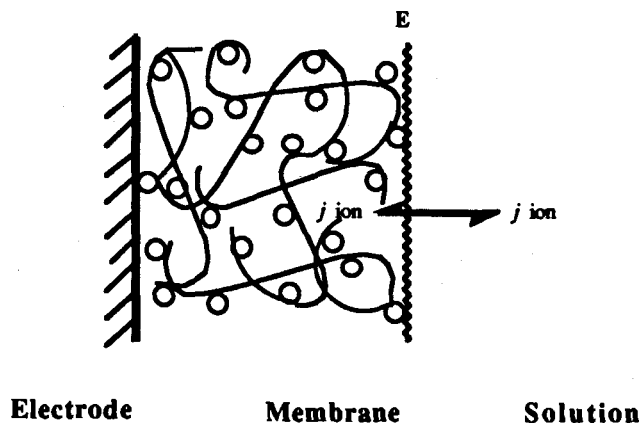
## PRELIMINARY INVESTIGATIONS OF ION-SELECTIVITY

As mentioned in Chapter 1, poly(crown ethers) have many potential applications. Polymers with pendent selenium coronands should also have potential uses as new sensor materials for ion-selective electrodes (ISEs). In this chapter the possibility of applying poly(selenium coronands) as an interface material for cation selective electrodes will be discussed.

### 4.1. Introduction

Until about 1965 the only ion-selective electrodes commercially available were the electrodes for the hydrogen ion (e.g. glass pH electrode) and sodium ion<sup>[76, 77]</sup>. Now there are specific-ion electrodes for more than 30 ions, including  $\text{Li}^+$ <sup>[78]</sup>,  $\text{K}^+$ <sup>[79]</sup>,  $\text{Na}^+$ <sup>[80]</sup>,  $\text{Rb}^+$ <sup>[81]</sup>,  $\text{Cs}^+$ <sup>[82]</sup>,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ <sup>[83]</sup>,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ <sup>[84]</sup>,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ <sup>[85-87]</sup>,  $\text{Pb}^{2+}$ <sup>[88, 89]</sup>,  $\text{Fe}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{UO}_2^{2+}$ <sup>[90]</sup>,  $\text{F}^-$ <sup>[91]</sup>,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_3^-$ <sup>[92]</sup>,  $\text{SO}_4^{2-}$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{HPO}_4^{2-}$ ; for several gases such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{HCN}$ ,<sup>[93, 94]</sup> and many organic ions, amino acids, alcohols, drugs<sup>[95-100]</sup>. The key part of an ISE is the ion-selective interface. Many ion-selective interfaces have been studied, and based on these, several different types of electrodes have been developed. Examples are glass electrodes, solid electrodes, membrane electrodes, enzyme electrodes, bacterial and tissue electrodes, and ion-based gas sensors.<sup>[94]</sup> In some cases,

combination electrodes are manufactured which combine a solid state ion-selective electrode and the reference electrode into a single sensor unit, capable of operating in a very small volume of solution. These have important medical and biochemical applications<sup>[101]</sup>. In addition to direct estimation of ions, specific-ion electrodes can be used for the detection of the equivalence point in the titration of ions. For example, the lead-sensitive electrode is used in the titration of sulfate (for which no ion-selective electrode is available yet) with lead nitrate solution. Another contribution of these electrodes is that they allow the construction of many cells without liquid junctions.



**Figure 26. Permselectivity of  $\text{Cu}^{2+}$  in the film of polymer modified electrode**

Among the applications of ion-selective electrodes, people have given the most attention towards liquid membrane type ISEs based on neutral carriers<sup>[102-105]</sup>. This is due to the ease of achieving high ion selectivity and

sensitivity by the use of specially synthesized ion-ligating compounds. Usually in these kinds of ISEs, the ion-selective membrane (interface) consists of a poly(vinyl chloride) (PVC) matrix containing an ion-selective species (or ion-selective sensor agents), a solvent mediator (plasticizer), a counter-ion excluder and some lipophilic additives. These membranes are used for detecting specific ions in solution. However, there are limitations with these kinds of ISEs, because they need a number of components in their construction. For example, the typical electrochemical assembly of these ISEs in their measurements are as follows [106-110]: [ AgCl, Ag | Internal solution | Solution to be investigated || ion-selective membrane || test solution | saturated KCl | AgCl, Ag ]. In recent years, because of the increasing demands for the application of ISEs in the fields of clinical and micro-analytical measurements of ions, the miniaturization of the ISEs is becoming very attractive. In order to accomplish this, modified wire electrodes have been developed by chemically or electrochemically coating an ion sensing layer on a small tip of electron conductor (electrode). Many efforts have been made in simplifying the above ISE assembly, such as coating a solid materials (e.g. polymer membranes) directly onto the surface of the electrode. Thus, a novel composition was made: [ Solid electrode | Ion-selective film | sample solution | Saturated KCl | AgCl, Ag ]. In fact, some cation-selective electrodes of this type have been constructed<sup>[96, 111-114]</sup>. Furthermore, membrane coated electrodes have been reported to improve the response time.<sup>[113]</sup> In this work, polymeric ligands (sensors) have been synthesized by selenium coronands covalently attached to polymer chain, and glassy carbon electrodes modified with these poly(selenium coronands) as sensor materials.

## 4.2. Principle of Ion-Selective Electrodes

All ISEs have essential selective membranes (interface). In these membranes, one of the ions is allowed to move, and if the activity of this ion in the solutions differs with that in the membrane, a potential difference will develop (Fig. 26). Under this situation, the chemical potential of particle  $j$  in the membrane and the solution may be written as

$$(\mu_j)_m = (\mu_j^\circ)_m + RT \ln (a_j)_m \quad (4-1)$$

$$(\mu_j)_s = (\mu_j^\circ)_s + RT \ln (a_j)_s \quad (4-2)$$

where  $(\mu_j)_m$  and  $(\mu_j)_s$  are the chemical potentials of the  $j$  ion in the membrane and in solution;  $(a_j)_m$  and  $(a_j)_s$  are the activities of the  $j$  ion in the membrane and solution, respectively<sup>[115]</sup>. Providing that  $E_m$  and  $E_s$  are the electrostatic potentials in the membrane phase and solution phase, the work that must be done to bring a mole of  $j$  ion from infinity into the interiors of the two phase are  $z_j F E_m$  and  $z_j F E_s$ . Thus, the electrochemical potential  $\mu^*$  (the total work) is the sum of chemical work ( $\mu$ ) and electrostatic work ( $zFE$ ):

$$\mu_m^* = (\mu_j)_m + z_j F E_m \quad (4-3)$$

$$\mu_s^* = (\mu_j)_s + z_j F E_s \quad (4-4)$$

In equilibrium,  $\mu_m^* = \mu_s^*$ ,<sup>[116]</sup> so

$$(\mu_j)_m + z_j F E_m = (\mu_j)_s + z_j F E_s \quad (4-5)$$

and

$$E = E_s - E_m = [(\mu_j)_m - (\mu_j)_s] / z_j F \quad (4-6)$$

where E is the potential difference between the membrane and solution. By introducing equation (4-1) and (4-2) to equation (4-6), we obtain

$$E = [(\mu_j^\circ)_m - (\mu_j^\circ)_s] / z_j F + RT / z_j F \ln [(a_j)_s / (a_j)_m] \quad (4-7)$$

if  $E^\circ$  is defined as  $E^\circ = [(\mu_j^\circ)_m - (\mu_j^\circ)_s] / z_j F$ , then the potential difference between the two phases can be given as<sup>[77, 117, 118]</sup>

$$E_m = E^\circ + \frac{RT}{Z_j F} \ln \frac{(a_j)_s}{(a_j)_m} \quad (4-8)$$

where R is gas constant, T is temperature in Kelvin, F is Faraday constant,  $Z_j$  is the charge of the j ion. Note that if the activity of species such as j is held constant in one phase (e.g. membrane phase), E will respond in a Nernstian fashion to the ion's activity in the other phase (equation 4-9). This idea is the essence behind the operation of ion-selective electrodes. Measurements with these devices are essentially determinations of potential difference between the two phases(Fig. 26).

$$E_m = E^{\circ'} + \frac{RT}{Z_j F} \ln (a_j)_s \quad (4-9)$$

Where E also called the electromotive force (EMF) of the electrochemical cell.  $E^{\circ'}$  is the EMF of the electrochemical cell with a solution in which  $a_j = 1$ .

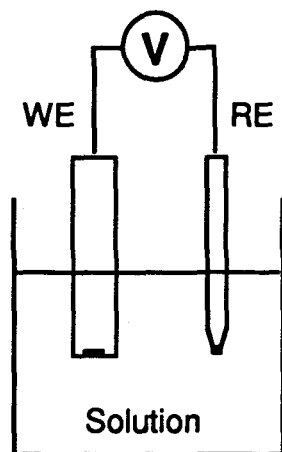


Figure 27. Cell assembly for EMF measurement

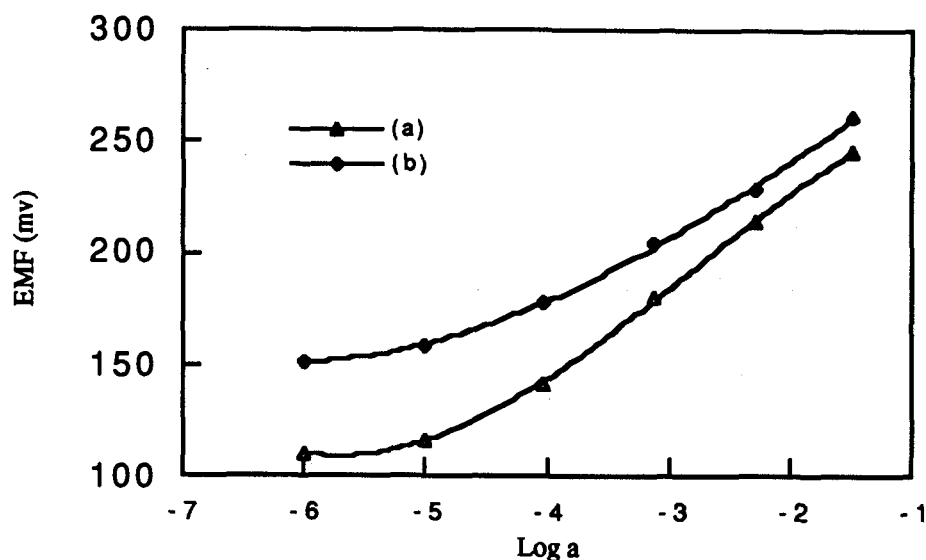
### 4.3. Results and Discussion

Experimental results shown in Fig. 28 are provided in the form of calibration graphs of ion-selective poly(selenium coronands) membrane electrodes. A Nernstian response to the log of activities of  $\text{Cu}^{2+}$  was obtained over a range of  $10^{-1}$  to  $10^{-4}$  M. The response time of the modified electrode to the change in ionic concentration was 20-30 sec. The EMF value became stable in 5 mins. The electrodes showed good reproducibility for repeated EMF measurements.

The selectivity coefficients ( $K_{\text{Cu}, \text{M}}^{\text{pot}}$ ) [116, 119] of modified electrodes for various cations were evaluated by the separate solution method. In this method, the potential of a cell comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing an ion A at the activity  $a_A$ , the other containing an ion B at the same activity  $a_B = a_A$ . If the measured values are  $E_1$  and  $E_2$ , respectively, the



selectivity coefficient ( $K_{A, B}^{pot}$ ) can be determined by the potential difference<sup>[116, 119]</sup>. A  $10^{-2}$  M activity of the cations, was used to calculate the selectivity coefficients in this experiment. The results are summarized in Fig. 28. From the results, we can see that poly(selenium coronands) is a potential sensor material to selectively detect  $Cu^{2+}$  ion over several common ions such as  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  cations. It can be seen from Fig. 29 that poly16Se4 coated electrode has a better selectivity than poly8Se2 coated electrode. This is consistent with UV-vis results described in the former Chapter. The potentiometric selectivity of the ISEs depends on the complexation specificity of the ligand molecules involved in the membrane. Complex formation and stability are the determining factors for selectivity and lifetime of the ISEs.



**Figure 28.** EMF response of polymer coated carbon electrodes to  $Cu^{2+}$  in solution. (a) poly8Se2 and (b) poly16Se4. Log a is the log of the activity of  $Cu^{2+}$ .

**Table 9. Physical data of metal ions in water solution**

		Data					
Concentration (M)		10 <sup>-1</sup>	10 <sup>-2</sup>	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-5</sup>	10 <sup>-6</sup>
Cu <sup>2+</sup>	I	4x10 <sup>-1</sup>	4x10 <sup>-2</sup>	4x10 <sup>-3</sup>	4x10 <sup>-4</sup>	4x10 <sup>-5</sup>	4x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.316	0.503	0.765	0.913	0.971	0.991
	Log a	-1.50	-2.30	-3.12	-4.04	-5.01	-6.00
Pb <sup>2+</sup>	I	3x10 <sup>-1</sup>	3x10 <sup>-2</sup>	3x10 <sup>-3</sup>	3x10 <sup>-4</sup>	3x10 <sup>-5</sup>	3x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.322	0.539	0.790	0.924	0.975	0.992
	Log a	-1.49	-2.27	-3.10	-4.03	-5.01	-6.00
K <sup>+</sup>	I	1x10 <sup>-1</sup>	1x10 <sup>-2</sup>	1x10 <sup>-3</sup>	1x10 <sup>-4</sup>	1x10 <sup>-5</sup>	1x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.795	0.905	0.965	0.989	0.996	0.999
	Log a	-1.10	-2.04	-3.02	-4.01	-5.00	-6.00
Na <sup>+</sup>	I	1x10 <sup>-1</sup>	1x10 <sup>-2</sup>	1x10 <sup>-3</sup>	1x10 <sup>-4</sup>	1x10 <sup>-5</sup>	1x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.795	0.905	0.965	0.989	0.996	0.999
	Log a	-1.10	-2.04	-3.02	-4.01	-5.00	-6.00
Ca <sup>2+</sup>	I	3x10 <sup>-1</sup>	3x10 <sup>-2</sup>	3x10 <sup>-3</sup>	3x10 <sup>-4</sup>	3x10 <sup>-5</sup>	3x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.322	0.539	0.790	0.924	0.975	0.992
	Log a	-1.49	-2.27	-3.10	-4.03	-5.01	-6.00
Mg <sup>2+</sup>	I	4x10 <sup>-1</sup>	4x10 <sup>-2</sup>	4x10 <sup>-3</sup>	4x10 <sup>-4</sup>	4x10 <sup>-5</sup>	4x10 <sup>-6</sup>
	$\gamma_{\pm}$	0.316	0.503	0.765	0.913	0.971	0.991
	Log a	-1.50	-2.30	-3.12	-4.04	-5.01	-6.00

Electrically neutral ligands have the capability to extract ions selectively from aqueous solutions into a hydrophobic membrane phase. Selenium

coronands have been demonstrated to be selective to some transition metal ions. They are expected to be suitable as neutral carriers and show potential as new sensor materials for ion-selective electrodes. In addition, covalent connection of these coronands with the polymer chain greatly reduces their toxicity and prevents their loss during the measurement. Furthermore, the fact that inter-molecular coupling reactions are inhibited, to a significant extent due to steric constraints (see previous Chapter), polymer-bound coronands may show enhanced stability compared to monomeric selenium coronands simply dispersed in a polymer matrix.

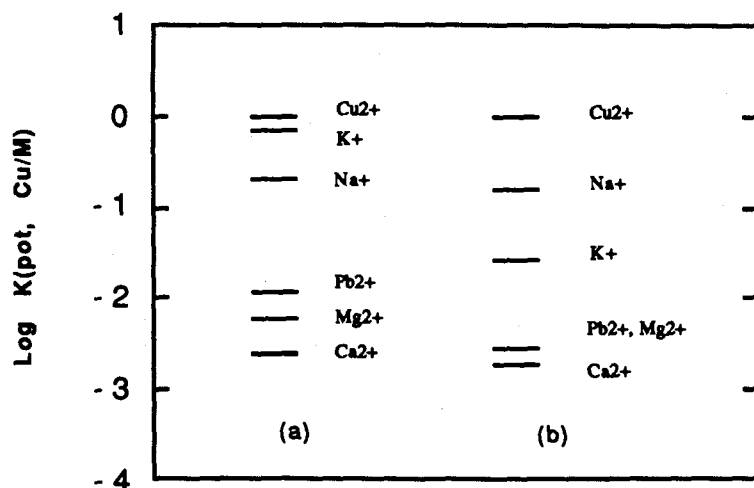


Fig. 29 Selectivity coefficients ( $K_{Cu, M}^{pot}$ ) for  $Cu^{2+}$  ion on carbon electrode coated with (a) poly8Se2 and (b) poly16Se4. The modified electrode was exposed to the solution of copper, lead, potassium, sodium, calcium, magnesium, respectively.

#### 4.4. Experimental

Poly(selenium coronands) films were cast onto polished glassy carbon disc electrodes (2.7 mm diameter) from dichloromethane. The modified working electrodes (WE) were conditioned before use by immersing them for 24 hrs in a  $1 \times 10^{-3}$  M solution of the appropriate primary ion. Electrodes were prepared with "fresh" membranes before detecting each kind of metal ion solutions. All potential measurements were performed with the following cell assembly: disc electrode/sensor membrane/sample solution/reference electrode (RE) as shown in Fig. 27. The potential was measured using a Fisher Scientific Accumet 910 digital PH meter. A saturated KCl-Ag/AgCl was used as a reference. The membrane electrode properties were determined by potential measurement on metal ion solution over a range of concentrations ( $10^{-1}$  to  $10^{-6}$  M) by serial dilution. Measurements were taken after 5 min of contact with each solution at room temperature. The metal ion solutions were freshly prepared by dilution from 0.1 M solution with deionized water. The activities (a) of metal ions (Table 9) were based on the activity coefficient ( $\gamma$ ) data calculated from the modified Debye-Huckel equation<sup>[120]</sup>:

$$\text{Log } \gamma_{\pm} = -0.511 z^2 [I^{1/2}/(1 + 1.5I^{1/2}) - 0.2I] \quad (4-10)$$

where I is the ionic strength and z is the valency.

# Chapter 5

## CONCLUSION

Polymerization of selenium coronands attached to acryloyl groups has yielded new kinds of polymers and copolymers with pendant selenium coronands. These polymers have shown different complexation ability and electrochemical activity compared to the corresponding monomeric selenium coronands. The polymers can form complexes with some transition metal ions although there does not appear to be a straight forward correlation with the principles of hard/soft acid/base theory. A cyclic voltammetric study of these polymers has suggested the existence of inter- and intra-selenium coronand reactions during the electrochemical process. Relative to monomeric selenium coronands, irreversible reactions between oxidized species and neutral ligands are suppressed by tethering the coronands to polymer chains. The polymers exhibit good selectivity and sensitivity towards  $\text{Cu}^{2+}$  in their use as sensor materials for ion-selective electrodes (ISEs).

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