

## CHAPTER 2

### EXPERIMENTAL SECTION

#### 2.1 General Procedure

##### 2.1.1 Analytical Instruments

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ACF 200 MHz nuclear magnetic resonance spectrometer. In all cases, samples were dissolved in deuterated chloroform and chemical shifts were recorded using a residual chloroform signal as an internal reference. UV-Visible Spectra were recorded on Spectronic 3000 ARRAY Spectrophotometer. Melting points were taken on an Electrothermal 9100 apparatus. Infrared spectra were carried out with Nicolet Impact 410 FT-IR Spectrometer.

Electrochemical measurement were performed using potentiostat PG100, with standard three-electrode cell : cyclic voltammetry was performed using a glassy carbon and Pt wire as working and reference electrode respectively, all the potentials refer to an Ag/AgCl reference electrode. Prior to use, the working electrode was polished with an aqueous suspension of 0.3  $\mu\text{m}$  alumina on a polishing pad. Solutions were deaerated by passing a current of nitrogen gas (5min) prior to each experiment.

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### 2.1.2 Materials

All reagents in standard analytical grade were purchased from Fluka, J.T. Baker and Merck and used without further purification. Commercial grade solvents such as dichloromethane, acetone, hexane and methanol were distilled before used.

Chromatography separations were performed on silica. (silica gel 60 Merck 7734) Thin layer chromatography (TLC) was carried out by silica plates. (Kieselgel 60 F<sub>254</sub>)

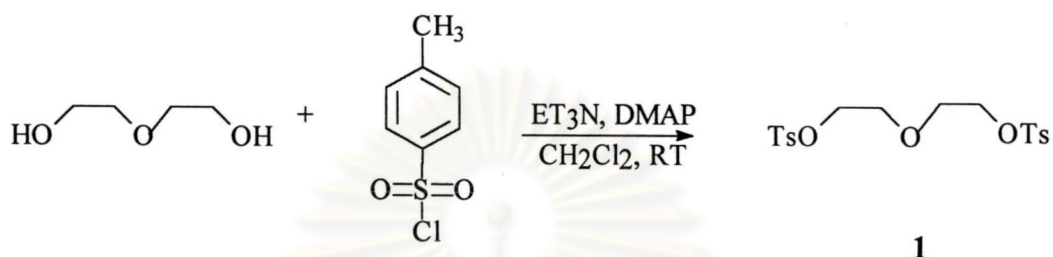


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## 2.2 Synthesis of polymeric salens.

### 2.2.1 Synthesis of polymeric diethyleneglycolic salen (7)

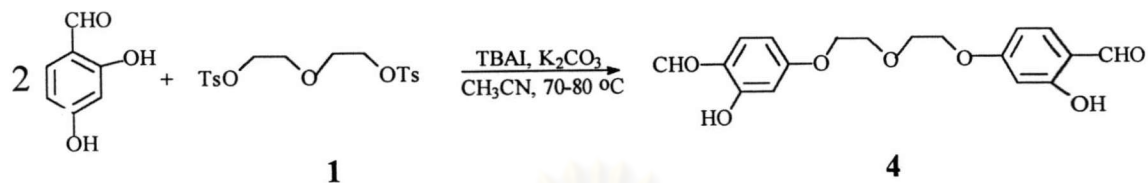
#### 2.2.1.1 Tosylate ester of diethyleneglycol (1)



A stirred mixture of diethylene glycol (5.0 mL, 52.5 mmol), triethylamine (15 mL) and DMAP (catalytic amount) in dry dichloromethane (50 mL) was cooled at 0 °C. Then, the solution of tosylchloride (20.0 g, 105.0 mmol) in dichloromethane (50 mL) was added dropwise and the reaction was allowed to warm to room temperature. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated off. Recrystallization in dichloromethane/ether afforded the desired product as a white solid (67% yield). TLC R<sub>f</sub> = 0.24 (hexane:ethylacetate = 70:30), <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.43 (2 ArCH<sub>3</sub>, s), 3.59 (2 CH<sub>2</sub>CH<sub>2</sub>O, t, J = 4.8 Hz), 4.07 (2 TsOCH<sub>2</sub>CH<sub>2</sub>, t, J = 4.6 Hz), 7.33 (4 ArH, d, J = 8.3 Hz), 7.76 (4 ArH, d, J = 8.3 Hz)

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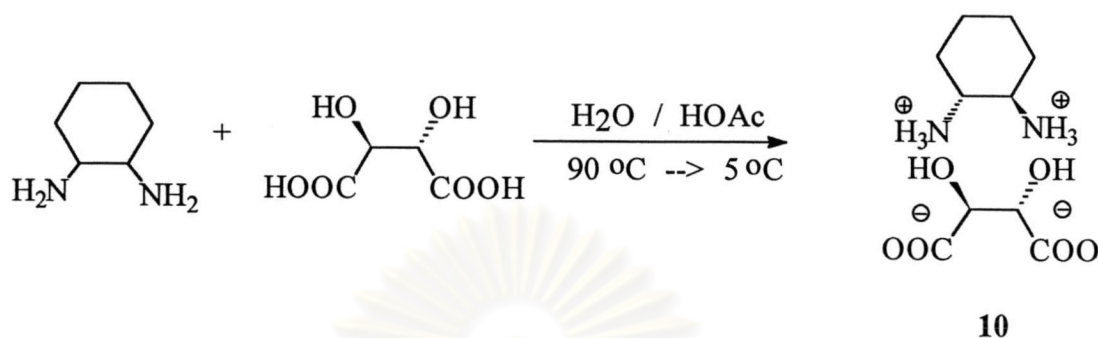
### 2.2.1.2 Diethyleneglycol bis(4-salicylyl)ether (4)



A stirred mixture of 2,4-dihydroxybenzaldehyde (2.0 g, 14.5 mmol), diethyleneglycol ditosylate (3.0 g, 7.3 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 g, 15.0 mmol) and tetrabutyl ammonium iodide (0.5 g, 1.5 mmol) in acetonitrile (50 mL) was heated at 70-80 °C for 24 hours under nitrogen atmosphere. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. The crude product was purified by column chromatography (hexane:ethylacetate = 70:30). Recrystallization in methanol/H<sub>2</sub>O yielded white solid as a product (58 % yield). TLC R<sub>f</sub> = 0.26 (hexane:ethylacetate = 70:30), <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>): δ 3.92 (2 OCH<sub>2</sub>CH<sub>2</sub>, t, J = 4.5 Hz), 4.16 (2 OCH<sub>2</sub>CH<sub>2</sub>, t, J = 2.5 Hz), 6.40 (2 ArH, d, J = 2.0 Hz), 6.52 (2 ArH, dd, J = 2.0 and 8.5 Hz), 7.38 (2 ArH, d, J = 8.5 Hz), 9.70 (2 ArCHO, s), 11.44 (2 ArOH, s)

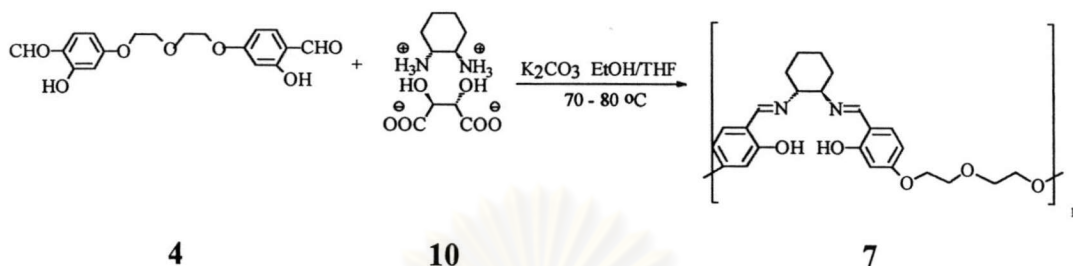
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### 2.2.1.3 Preparation of (*R,R*)-diaminocyclohexane tartrate salt (**10**)<sup>16</sup>



A 500 mL beaker was charged with L-(+)-tartaric acid (25.0 g, 166.5 mmol) and distilled water (60 mL). The mixture was stirred at room temperature until complete dissolution occurred, then a mixture of *cis*- and *trans*-1,2-diaminocyclohexane (40 mL, 325.7 mmol) was added at a rate such that the reaction temperature just reached 70 °C. To the resulting solution was added glacial acetic acid (16.7 mL, 0.3 mmol) at a rate such that the reaction temperature just reached 90 °C. White precipitate formed immediately upon the addition of the acid and the slurry was vigorously stirred while it was cooled to room temperature over 2 hours. The mixture was then cooled to 5 °C with an ice bath for 2 hours and the precipitate was collected by vacuum filtration. The wet cake was washed with cool water (20 mL) and then rinsed with methanol (5 x 20 mL). The solid was dried by drawing air through the filter cake for 1 hours. The product was then dried at 40 °C under reduced pressure to yield (*R,R*)-1,2-diaminocyclohexane mono-(+)-tartrate salt as a white solid.

### 2.2.1.4 Preparation of polymeric diethyleneglycol salen (7)

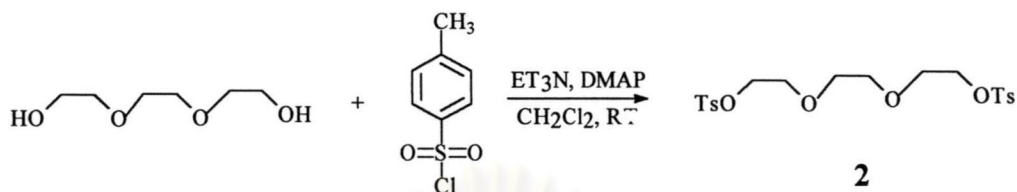


The stirred mixture of diethyleneglycol bis(4-salicylyl) ether (0.5 g, 1.5 mmol) (*R,R*)-*trans*-1,2-diaminocyclohexane mono-(+)-tartrate salt (0.4 g, 1.5 mmol) and  $K_2CO_3$  (0.2 g, 1.5 mmol) in ethanol (10 mL) was heated at 70-80 °C. After the polymer precipitated, ethanol was removed and then THF (10 mL) was added as solvent. The reaction mixture was heated at 70-80 °C for 24 hours. Then, the volume of the reaction mixture was reduced to one half by evaporation and the reaction mixture was poured into an excess amount of methanol. The product was filtered and dried under vacuo. The product was obtained as a yellow solid (79 % yield). The structure of the product was confirmed by  $^1H$ -NMR.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  1.40-1.86 (4 cyclic  $CH_2$ , broad), 3.16 (2 cyclic  $CH$ , broad), 3.81 (2  $OCH_2CH_2$ , broad), 4.02 (2  $OCH_2CH_2$ , broad), 6.24-6.30 (4 ArH, m), 6.93 (2 ArH, d,  $J = 8.5$  Hz) 8.01 (2 ArCH=N, s), 13.77 (2 ArOH, broad)

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## 2.2.2 Synthesis of polymeric triethyleneglycolic salen (8)

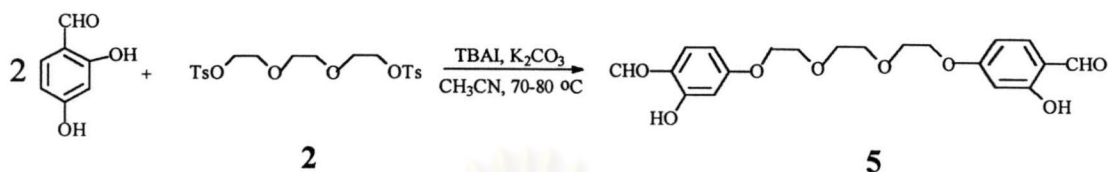
### 2.2.2.1 Tosylate ester of triethyleneglycol (2)



A stirred mixture of triethylene glycol (7.0 mL, 52.0 mmol), triethylamine (15 mL) and DMAP (catalytic amount) in dry dichloromethane (50 mL) was cooled at 0 °C. Then, the solution of tosylchloride (20.0 g, 105.0 mmol) in dichloromethane (50 mL) was added dropwise and reaction was allowed to warm to room temperature. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. Recrystallization in dichloromethane/ether afforded the desired product as a white solid (73% yield). TLC  $R_f = 0.11$  (hexane:ethylacetate = 70:30), <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.43 (2 ArCH<sub>3</sub>, s), 3.61 (2 CH<sub>2</sub>OCH<sub>2</sub>, s), 3.64 (2 CH<sub>2</sub>OCH<sub>2</sub>O, t,  $J = 5.0$  Hz), 4.10 (2 TsOCH<sub>2</sub>CH<sub>2</sub>, t,  $J = 3.0$  Hz), 7.30 (4 ArH, d,  $J = 8.5$  Hz), 7.76 (4 ArH, d,  $J = 8.0$  Hz)

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### 2.2.2.2 Triethyleneglycol bis (4-salicylyl)ether (5)

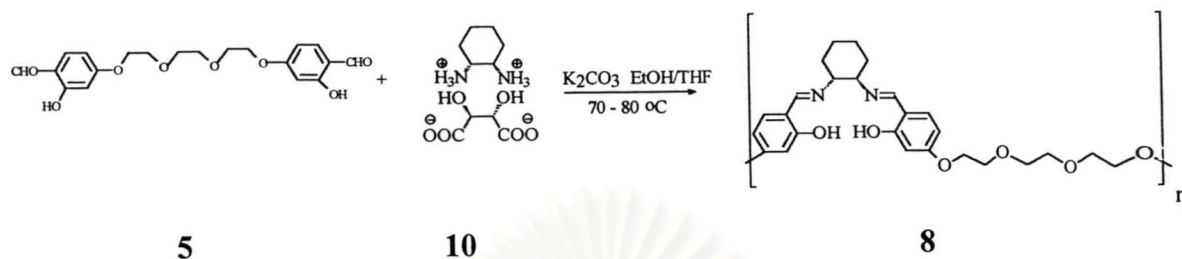


A stirred mixture of 2,4-dihydroxybenzaldehyde (2.0 g, 14.5 mmol), triethyleneglycol ditosylate (3.3 g, 7.3 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 g, 15.0 mmol) and tetrabutyl ammonium iodide (0.5 g, 1.5 mmol) in acetonitrile (50 mL) was heated at 70-80 °C for 24 hours under nitrogen atmosphere. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. The crude product was purified by column chromatography (hexane:ethylacetate = 70:30). Recrystallization in methanol/H<sub>2</sub>O yielded white solid as a product (32% yield). TLC R<sub>f</sub> = 0.13 (hexane:ethylacetate = 70:30), <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>): δ 3.85 (4 OCH<sub>2</sub>, s), 3.86 (4 OCH<sub>2</sub>CH<sub>2</sub>, t, J = 5.0 Hz), 4.13 (4 OCH<sub>2</sub>CH<sub>2</sub>, t, J = 5.0 Hz), 6.41 (2 ArH, d, J = 2.0 Hz), 6.51 (2 ArH, dd, J = 2.0 and 8.5 Hz), 7.37 (2 ArH, d, J = 8.5 Hz), 9.68 (2 ArCHO, s), 11.48 (2 ArOH, s)

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### 2.2.2.3 Preparation of polymeric triethyleneglycolic salen (8)

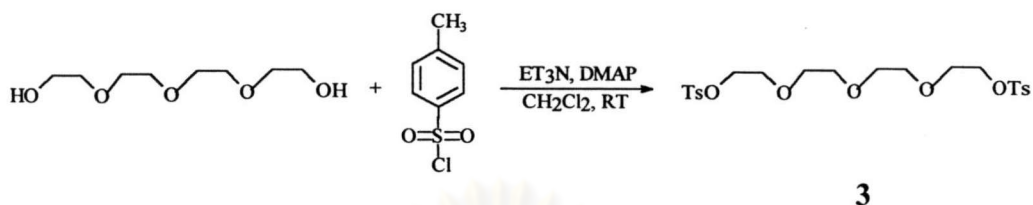


The stirred mixture of triethyleneglycol bis(4-salicylyl) ether (0.5 g, 1.3 mmol) (*R,R*)-*trans*-1,2-diaminocyclohexane mono-(+)-tartrate salt (0.3 g, 1.3 mmol) and  $K_2CO_3$  (0.2 g, 1.3 mmol) in ethanol (10 mL) was heated at 70-80 °C. After the polymer precipitated, ethanol was removed and then THF (10 ml) was added as solvent. The reaction mixture was heated at 70-80 °C for 24 hours. Then, the volume of the reaction mixture was reduced to one half by evaporation and the reaction mixture was poured into an excess amount of methanol. The product was filtered and dried under vacuo. The product was obtained as a yellow solid (81 % yield).  $^1H$ -NMR spectrum ( $CDCl_3$ ): $\delta$  1.40-1.86 (4 cyclic  $CH_2$ , broad), 3.17 (2 cyclic  $CH$ , broad), 3.67 (2  $OCH_2CH_2$ , broad), 4.03 (2  $OCH_2CH_2$ , broad), 6.30 (2  $ArH$ , d,  $J = 2.0$  Hz), 6.96 (2  $ArH$ , d,  $J = 8.5$  Hz), 8.05 (2  $ArCH=N$ , s), 11.48 (2  $ArOH$ , broad)

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### 2.2.3 Synthesis of polymeric tetraethyleneglycolic salen (9)

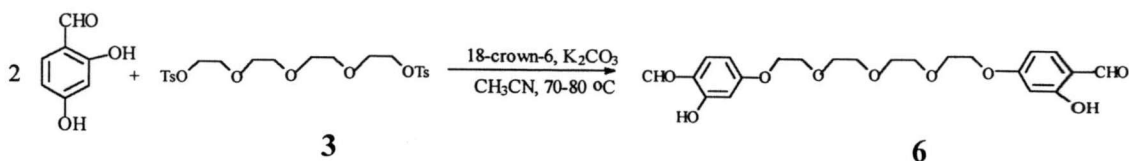
#### 2.2.3.1 Tosylate ester of tetraethyleneglycol (3)



A stirred mixture of tetraethylene glycol (9.1 mL, 52.5 mmol), triethylamine (15 mL) and DMAP (catalytic amount) in dry dichloromethane (50 mL) was cooled at 0 °C. Then, the solution of tosylchloride (20.0 g, 105.0 mmol) in dichloromethane (50 mL) was added dropwise and reaction was allowed to warm to room temperature. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. The crude product was purified by column chromatography (hexane:ethylacetate = 70:30). The colorless oil was obtained as a product (71% yield). TLC R<sub>f</sub> = 0.20 (hexane:ethylacetate = 60:40), <sup>1</sup>H-NMR(CDCl<sub>3</sub>): δ 2.42 (2 ArCH<sub>3</sub>, s), 3.50 (2 OCH<sub>2</sub>CH<sub>2</sub>, s), 3.63 (2 OCH<sub>2</sub>CH<sub>2</sub>O, t, J = 4.5 Hz), 4.10 (2 OCH<sub>2</sub>CH<sub>2</sub>O, t, J = 4.5 Hz), 7.29 (4 ArH, d, J = 8.5 Hz), 7.74 (4 ArH, d, J = 8.5 Hz)

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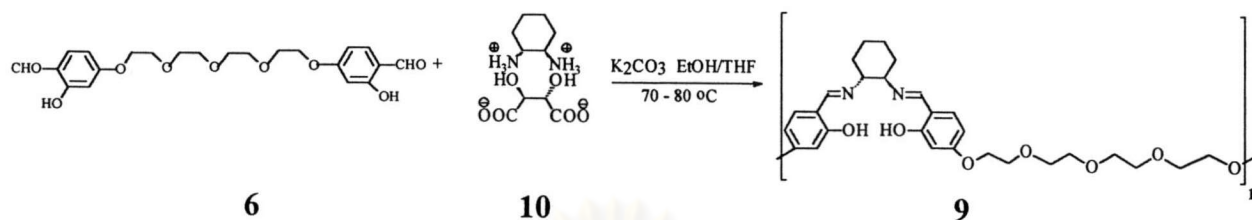
### 2.2.3.2 Tetraethyleneglycol bis(4-salicylyl)ether (6)



A stirred mixture of 2,4-dihydroxybenzaldehyde (2.0 g, 14.5 mmol), tetraethyleneglycol ditosylate (3.6 g, 7.3 mmol),  $K_2CO_3$  (2.0 g, 15.0 mmol) and 18-crown-6 (0.38 g, 1.44 mmol) in acetonitrile (50 mL) was heated at 70-80 °C for 24 hours under nitrogen atmosphere. The reaction was monitored by TLC. After the reaction was completed, the solution was then poured into 2 M hydrochloric acid (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic extract was dried over  $Na_2SO_4$  and the solvent was removed. The crude product was purified by column chromatography (hexane:ethylacetate = 70:30) yielded colorless liquid as a product (13 % yield). TLC  $R_f$  = 0.16 (hexane:ethylacetate = 60:40),  $^1H$ -NMR ( $CDCl_3$ ): $\delta$  3.81 (2  $OCH_2CH_2$ , s), 3.82 ( $OCH_2CH_2$ , t,  $J$  = 5.0 Hz), 4.11 (2  $OCH_2CH_2$ , t,  $J$  = 5.0 Hz), 6.49 (2 ArH, s), 6.50 (2 ArH, dd,  $J$  = 2.5 Hz,  $J$  = 8.5 Hz), 9.68 (2 ArCHO, s), 11.44 (2 ArOH, s)

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### 2.2.3.3 Preparation of polymeric tetraethyleneglycolic salen (9)

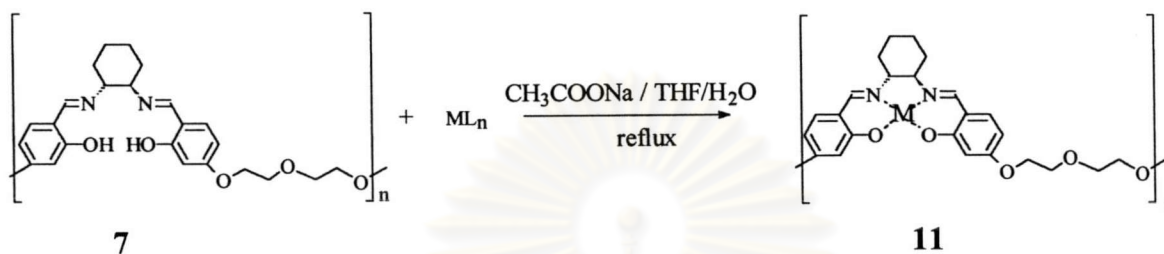


The stirred mixture of tetraethyleneglycol bis (4-salicylyl) ether (0.5 g, 1.2 mmol), (*R,R*)-*trans*-1,2-diaminocyclohexane mono-(+)-tartrate salt (0.3 g, 1.2 mmol) and  $K_2CO_3$  (0.2 g, 1.2 mmol) in ethanol (10 mL) was heated at 70-80 °C. After the polymer precipitated, ethanol was removed and then THF (10 mL) was added as solvent. The reaction mixture was heated at 70-80 °C for 24 hours. Then, the volume of the reaction mixture was reduced by evaporation and the reaction mixture was poured into an excess amount of methanol. The product was filtered and dried under vacuo. The product was obtained as a yellow solid (83% yield).  $^1H$ -NMR ( $CDCl_3$ ): $\delta$  1.40-1.86 (4 cyclic  $CH_2$ , broad), 3.17 (2 cyclic  $CH$ , broad), 3.67 (2  $OCH_2$ , broad), 3.70 (2  $CH_2CH_2O$ , broad), 4.01 (2  $OCH_2CH_2$ , broad), 6.26 (2  $ArH$ , d,  $J = 8.50$  Hz), 6.92 (2  $ArH$ , d,  $J = 8.0$  Hz), 8.05 (2  $ArCH=N$ , s), 9.68 (2  $ArCHO$ , s), 11.48 (2  $ArOH$ , broad)

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### 2.3 Complexation studies and their solubility tests.

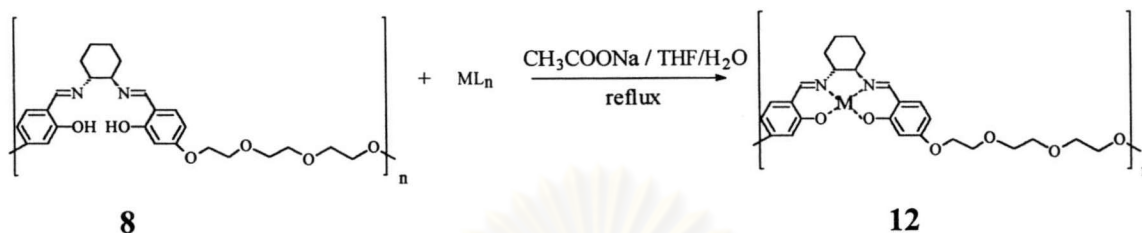
#### 2.3.1 The complexation reaction of polymeric diethyleneglycolic salen with $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{V}^{4+}$ and $\text{Mn}^{2+}$ ions. (11)



A solution of polymeric diethyleneglycolic salen (0.1 g, 0.2 mmol) in THF (10 mL) was mixed with an aqueous (5 mL) solution of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{VOSO}_4$  or  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.2 mmol) and  $\text{CH}_3\text{COONa}$  (0.5 mmol). A precipitation was observed immediately. The reaction mixture was heated at reflux for 3 hours and then stirred at room temperature overnight. The solid was filtered and washed with  $\text{H}_2\text{O}$ , EtOH and ether, respectively. The resulting solid was dried under vacuum to give the polymeric salen complexes. The solubility in various solvents of all complexes was examined.

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**2.3.2 The complexation reaction of polymeric triethyleneglycolic salen with Ni<sup>2+</sup>, Co<sup>2+</sup>, V<sup>4+</sup> and Mn<sup>2+</sup> ions. (12)**



A solution of polymeric triethyleneglycolic salen (0.1 g, 0.2 mmol) in THF (10 mL) was mixed with an aqueous (5 mL) solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O or Co(OAc)<sub>2</sub>·4H<sub>2</sub>O or VOSO<sub>4</sub> or Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.2 mmol) and CH<sub>3</sub>COONa (0.5 mmol). The reaction mixture was heated at reflux for 3 hours and then stirred at room temperature overnight. In case of the complexation reaction of polymeric triethyleneglycolic salen with Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, the reaction remained homogenous. Therefore, the reaction mixture was allowed to cool to room temperature and then brine (20 mL) was added. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was collected and evaporated. The brown solid was obtained. Unlike the manganese complex, the complexes of Ni<sup>2+</sup>, Co<sup>2+</sup> and V<sup>4+</sup> precipitated out during the reaction. In these cases, the precipitates were filtered and washed with H<sub>2</sub>O, EtOH and ether respectively. All products were dried under vacuo. The solubility in various solvents of all complexes were examined.

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**2.3.3 The complexation reaction of polymeric tetraethyleneglycolic salen with  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{V}^{4+}$  and  $\text{Mn}^{2+}$  ions. (13)**



A solution of polymeric tetraethyleneglycolic salen (0.1 g, 0.2 mmol) in THF (10 mL) was mixed with an aqueous (5 mL) solution of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{VOSO}_4$  or  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.2 mmol) and  $\text{CH}_3\text{COONa}$  (0.5 mmol). The reaction mixture was heated at reflux for 3 hours and then stirred at room temperature for overnight. In case of the complexation reaction of polymeric tetraethyleneglycolic salen with  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , the reaction remained homogenous. Therefore, the reaction mixture was allowed to cool to room temperature and then brine (20 mL) was added. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was collected and evaporated. The brown solid was obtained. Unlike manganese complex, the complexes of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{V}^{4+}$  precipitated out during the reaction. In these cases, the precipitates were filtered and washed with  $\text{H}_2\text{O}$ , EtOH and ether respectively. All products were dried under vacuum. The solubility in various solvents of all complexes was examined.

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## 2.4 The determination of degree of complexation by Atomic Absorption Spectroscopy (AAS)

The degree of complexation were determined by standard addition method to avoid the matrix interference. Flame Atomization Technique was performed by using air/acetylene as the flame.

### 2.4.1 Standard preparation

$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.0254 g) and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.0244 g) were transferred into 100 mL volumetric flasks and then distilled water was added to the mark to give  $10^{-3}$  M standard solution.

### 2.4.2 Sample preparation

$(\text{Ni}-(\text{EG})_4\text{sal})_n$  (0.0092 g) and  $(\text{Mn}-(\text{EG})_4\text{sal})_n$  (0.0067 g) were added with 1 mL  $\text{HNO}_3(\text{conc})$  and gently heated to dissolve the complexes. The solution was transferred into 100 mL volumetric flasks and then water was added to the mark to give  $10^{-4}$  M sample solution.

### 2.4.3 Sample preparation for standard addition method

The standard solution (0,1,2,3 and 4 mL) was transferred into 100 mL volumetric flasks and then 10 mL of sample solution was added into each flask. The volume was adjusted to the mark with distilled water to give approximate  $10^{-5}$  M sample solution. All aliquats of samples were filtered before the measurement of the absorption.

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## 2.5 Electrochemical Studies

### 2.5.1 Apparatus

#### Aqueous system

Platinum electrode, Ag/AgCl (saturated with KCl solution) and platinum coil were used as a working electrode, a reference electrode and an auxiliary electrode, respectively. Phosphate-buffered solution (PBS, pH 7.4) was used as a buffer.

#### Non-aqueous system

Glassy carbon electrode, Ag/AgCl and platinum wire were used as a working electrode, a reference electrode and an auxiliary electrode, respectively. Tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile was used as an electrolyte. AgNO<sub>3</sub> (0.1 M) was used as an internal standard. To avoid the interference from O<sub>2</sub>, the electrolyte was bubbled with N<sub>2</sub> (5 min) before each measurement.

### 2.5.2 Electrode Preparation

The studied complex (5 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 μL) and then the complex solution (5 μL) was coated on the working electrode. The modified electrode was left in the open air for the solvent evaporation. The similar preparations were performed in every cyclic voltammetric experiments.

### 2.5.3 Effect of the electrolytes

To find out the suitable condition for cyclic voltammetry, both aqueous and non-aqueous conditions were utilized. The cyclic voltammetry was measured at the scan rate of 0.2 mV/s by using metal-salen modified electrode as a working electrode. The suitable condition was justified from the appearance of signals in the voltammograms.

#### 2.5.4 Sensitivity of the metal-salen modified electrode to the selected analytes

The analytes tested in this work were methanol, styrene oxide, pyridine, methylbenzylamine and (*R,R*) and (*S,S*)-1,2-diaminocyclohexane. The cyclic voltammetry using modified electrodes was performed in the non-aqueous electrolyte containing 200  $\mu\text{L}$  methanol ( $5.00 \times 10^{-2}$  M), styrene oxide ( $1.76 \times 10^{-1}$  M), pyridine ( $2.48 \times 10^{-1}$  M) methylbenzylamine ( $1.57 \times 10^{-1}$  M) and (*R,R*) and (*S,S*)-1,2-diaminocyclohexane ( $1.00 \times 10^{-3}$  M). The cyclic voltammograms of modified metal salen electrode both in the presence and absence of analytes were compared.

#### 2.5.5 The linear range of modified electrode to the analytes

The linear range of analytes were obtained from the measurement of either the shift of oxidation current of the electrode's signal or the increasing of oxidation current of the analytes resulting from the successive addition of the analytes in acetonitrile containing TBAP by using metal salen coated electrode as working electrode.

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