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Communications

An Electrochemical Sensor from a Soluble Polymeric Ni−salen Complex

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Introduction

Owing to their ability to complex with a wide variety of transition metal ions, salens have become one of the most widely studied groups of ligands. Various applications of the metal−salen complexes have been demonstrated such as asymmetric catalysis,[1] sensing,[2] DNA cleavage,[3] and optoelectronics.[4] Incorporation of metal−salen complexes into a polymeric system offered some advantages in certain applications.[5] The rigidity of the structure of the metal−salen complexes has been a major reason for the insolubility of these polymeric materials in common solvents, thus encumbering the desirable simple fabrication of the polymers. Furthermore, most of the key structural information such as averaged molecular weights and backbone structures cannot be obtained from the insoluble polymers. Interpretations of the operational mechanisms of devices fabricated from such insoluble polymers are, therefore, often precarious. To increase the solubility of the rigid salen moieties, the incorporation of a flexible chain into salen polymers has been studied in our group. We found that a polymer containing a flexible long alkyl chain was soluble in THF, DMF, and chlorinated solvents.[6] However, the complexation between these soluble polymers and transition metal ions led to insolubility. In recent years, polymer functionalization has been one of the most effective means used for the synthesis of novel soluble polymers with interesting photonic and electronic properties.[7] Using this synthetic paradigm, we report here a successful synthesis of new soluble polymeric metal−salen complexes with interesting electrochemical properties for sensing applications.

The newly designed soluble salen polymers (**1**, **2**, and **3**) contain various lengths of glycolic chains between the chiral salen units. They were prepared from a condensation between the corresponding bis-salicylaldehydes and *trans*-diaminocyclohexane (Scheme 1).

The polymerization was initially carried out in ethanol to facilitate the dissolution of the amine tartrate salt until the precipitation of the polymer occurred when the ethanol was evaporated and replaced by THF. The precipitated polymer was redissolved in THF and the

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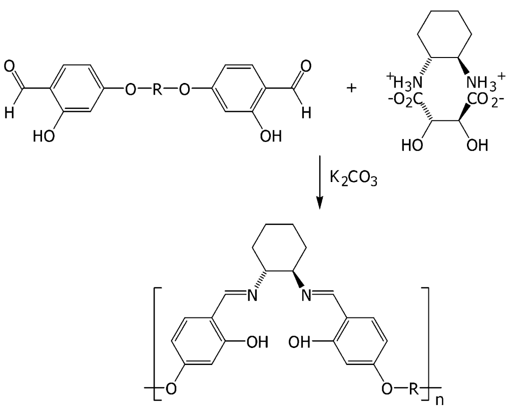
Scheme 1



1 R = $CH_2CH_2OCH_2CH_2$ 79% yield
2 R = $CH_2CH_2OCH_2CH_2OCH_2CH_2$ 81% yield
3 R = $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2$ 83% yield

condensation polymerization continued to produce a polymer with acceptable molecular weight. This polymerization gave the desired polymers after precipitation in methanol in 79−83% yields.[8]

All three synthesized polymers were soluble in common organic solvents as designed and their averaged molecular weights were determined from their solutions in THF by gel-permeation chromatography (GPC) calibrated with polystyrene standards to provide M_n and M_w (Table 1). With their good solublity in chloroform, the ^1H and ^{13}C NMR spectra of these polymers were also readily obtained. The number of repeating units of these polymers was calculated from M_n and compared with those obtained from the integral ratio of the ^1H NMR signals, corresponding to the terminal iminic protons and the internal iminic protons. The number of repeating units calculated from ^1H NMR spectra were significantly greater than those derived from M_n. We speculated that some cyclic structures might be formed during the polymerization. There have been reports of cyclization in the preparation of salen derivatives with similar structures.[6,9] These cyclic oligomers, lacking a chain terminus, contribute to the diminishing of the peak area of the terminal iminic proton signals and cause the increase in the number of repeating units estimated from the ^1H NMR spectra.

Complexation of these soluble polymeric salens with transition metal ions (Ni^{2+}, Mn^{3+}, Co^{2+}, and V^{4+}) was performed in aqueous THF solutions. The solubilities of all polymeric complexes were evaluated (Table 2). The complexes of polymer **1** with all four metal ions were not soluble in any common organic solvent. As expected, increasing the flexible glycolic chain length increased the solubility of these complexes. The complexes of polymeric salens containing the tri- and tetraethylene glycolic chains (polymers **3** and **4)** with Ni^{2+}, Mn^{3+}, and V^{4+} were soluble in some organic solvents such as THF, DMF, and chlorinated solvents. However, Co^{2+} complexes of polymeric salens remained insoluble in all tested solvents, although the glycolic chain lengths were increased. The insolubility of these Co^{2+} complexes is probably due to the preferred octahedral coordination of the Co^{2+} ions. The oxygen atoms of the glycolic chain may act as axial ligands binding strongly to Co^{2+}, resulting in highly cross-linked structures.

Table 1. Average Molecular Weights and the Numbers of Repeating Units of the Polymeric Salens

	GPC analysis		number of repeating units (*n*)	
polymer	M_n	M_w	from M_n	from ^1H NMR
1	5100	12300	12	27
2	5250	9980	11	21
3	17500	20800	34	*a*

[a] ^1H NMR of tetraethyleneglycolic polymeric salen showed no signal for a chain terminal proton.

Table 2. Solubility Behavior of All Complexes

	solubility			
polymer	Ni^{2+}	Mn^{3+}	Co^{2+}	V^{4+}
1	×	×	×	×
2	√	√	×	√
3	√	√	×	√

[a] √: soluble in CH_2Cl_2 THF. ×: insoluble in common organic solvents

The Ni^{2+} complex of polymer **3** was selected for further study as a potential electrochemical sensor by cyclic voltammetry. The degree of metal complexation of this polymer, determined by atomic absorption spectroscopy, was virtually 100%, meaning that every salen unit in the polymer chain contained Ni^{2+}. In the electrochemical study, a modified electrode was prepared by casting a solution of the polymer complex on the surface of a glassy carbon working electrode.[10] Thanks to its good solubility, the polymeric Ni^{2+} salen complex (polymer **3**) was conveniently and neatly coated onto the surface of the electrode as a thin film. Cyclic voltammetry (scan rate 0.20 V/s) was performed in acetonitrile in the presence of tetrabutylammonium perchlorate electrolyte (0.1 M) and $AgNO_3$ (0.1 M) as an internal standard. A Ag/AgCl electrode and a Pt wire were used as reference and auxiliary electrodes, respec-

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(8) A stirred mixture of the corresponding dialdehyde monomers (1.30 mmol), (*R*,*R*)-*trans*-1,2-diaminocyclohexane mono-(+)-tartrate salt (1.30 mmol), and K_2CO_3 (1.30 mmol) in ethanol (10 mL) was refluxed. After the precipitation of the polymer was observed, ethanol was evaporated off and THF (10 mL) was then added as a new solvent. The reaction mixture was reheated to reflux for 24 h. After the reaction mixture was allowed to cool to room temperature, the volume was reduced to one-half by evaporation and was poured into an excess amount of methanol. The product was filtered and dried under vacuum. The product was obtained as a yellow solid (78−83% yield). **Polymer 1**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.40−1.86 (8 cyclic CH_2, a group of four broad signals), 3.16 (2 cyclic C*H*, broad), 3.81 (2 CH_2OCH_2, broad), 4.02 (2 CH_2OAr, broad), 6.28 (4 Ar*H*, m), 6.93 (2 Ar*H*, d, $J = 8.5$ Hz), 8.01 (2 ArC*H*=N, s), 13.77 (2 ArO*H*, broad); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2 (2 cyclic CH_2), 33.0 (2 cyclic CH_2), 67.4 (2 cyclic *C*H), 69.6 (2 CH_2OCH_2), 71.4 (2 CH_2OAr), 101.8 (2 Ar. CH), 106.7 (2 Ar. CH), 112.3 (2 Ar. C), 132.8 (2 Ar. CH), 162.5 (2 Ar. C), 163.8 (CH=N), 165.0 (2 Ar. C). Anal. Calcd for $C_{24}H_{28}N_2O_5$: C, 67.92; H, 6.60; N, 6.60. Found: C, 65.82; H, 6.84; N, 5.36. **Polymer 2**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.40−1.86 (8 cyclic CH_2, a group of four broad signals), 3.17 (2 cyclic C*H*, broad), 3.67 (6 CH_2OCH_2, broad), 4.03 (2 CH_2OAr, broad), 6.30 (4 Ar*H*, m), 6.96 (2 Ar*H*, d, $J = 8.5$ Hz), 8.05 (2 ArC*H*=N, s), 11.48 (2 ArO*H*, broad); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2 (2 cyclic CH_2), 33.0 (2 cyclic CH_2), 67.4 (2 cyclic *C*H), 69.5 (2 CH_2OCH_2), 70.8 (2 CH_2OCH_2), 71.4 (2 CH_2OAr), 101.8 (2 Ar. CH), 106.7 (2 Ar. CH), 112.3 (2 Ar. C), 132.8 (2 Ar. CH), 162.6 (2 Ar. C), 163.8 (CH=N), 164.9 (2 Ar. C). Anal. Calcd for $C_{26}H_{32}N_2O_6$: C, 66.67; H, 6.84; N, 5.98. Found: C, 63.43; H, 7.84; N, 5.69. **Polymer 3**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.40−1.86 (8 cyclic CH_2, a group of four broad signals), 3.17 (2 cyclic C*H*, broad), 3.67 (2 OCH_2, broad), 3.70 (2 CH_2CH_2O, broad), 4.01 (2 OCH_2CH_2, broad), 6.26 (2 Ar*H*, d, $J = 8.50$ Hz), 6.92 (2 Ar*H*, d, $J = 8.0$ Hz), 8.05 (2 ArC*H*=N, s), 9.68 (2 ArC*H*O, s), 11.48 (2 ArO*H*, broad); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2 (2 cyclic CH_2), 33.0 (2 cyclic CH_2), 67.3 (2 cyclic *C*H), 69.4 (2 CH_2OCH_2), 70.6 (2 CH_2OCH_2), 70.8 (2 CH_2OCH_2), 71.4 (2 CH_2OAr), 101.7 (2 Ar. CH), 106.7 (2 Ar. CH), 112.3 (2 Ar. C), 132.8 (2 Ar. CH), 162.6 (2 Ar. C), 163.8 (CH=N), 164.9 (2 Ar. C). Anal. Calcd for $C_{28}H_{36}N_2O_7$: C, 65.63; H, 7.03; N, 5.47. Found: C, 64.46; H, 6.35; N, 5.37.

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(10) The studied complex (5 mg) was dissolved in CH_2Cl_2 (100 μL) and the complex solution (5 μL) was cast onto the glassy carbon working electrode (diameter 3 mm). The modified electrode was left in the open air for solvent evaporation.

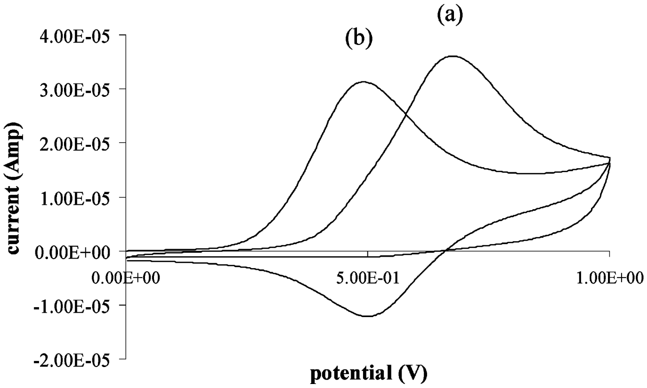

Figure 1. Cyclic voltammogram of the electrode coated with Ni(II)−**polymer 3** complex in the (a) absence and (b) presence of pyridine (2.48×10^{-1} M).

tively. The signals corresponding to a semi-reversible oxidation−reduction of Ni^{2+} were observed when the coated electrode was used as a working electrode (Figure 1 a) whereas the cyclic voltammogram of the unmodified conventional glassy carbon working electrode showed no signal. These results confirmed the attachment of the polymeric Ni^{2+} salen complex on the electrode. It is of interest to note here that the Mn^{3+} and V^{4+} metal complexes of polymer **3** gave only weak and irreversible oxidation−reduction signals. We therefore selected the Ni^{2+} polymeric salen complex for further investigation.

Generally, a tetradentate salen ligand occupies four coordination sites on Ni^{2+}, leaving one or two coordination sites for more labile ligands. As a result, an appropriate organic compound containing a donor atom with lone pair electrons should be able to bind at these free coordination sites, resulting in a change of the electronic environment of the complex and a change of the voltammetric signal. The change in voltammetric signal should allow electrochemical detection of such organic compounds in solution. We chose pyridine as an analyte to demonstrate this concept. The cyclic voltammetry was performed again in the same nonaqueous electrolyte in the presence of pyridine (2.48×10^{-1} M). The cyclic voltammogram in the presence of pyridine displayed the anodic signal at 0.48 V, significantly shifted from the signal at 0.66 V which appeared in the absence of pyridine (Figure 1). Disappointingly, the cathodic wave of the modified electrode also disappeared in the presence of pyridine, suggesting that the modified electrode can be used only once, as the electrochemical process was irreversible. Indeed, the second scan on this electrode in the presence of pyridine did not give any voltammetric signal.

The following electrochemical process was hypothesized to account for the observations. First, the shift of oxidation signal may result from a binding of pyridine at the free axial sites of Ni^{2+}as aforementioned. The basicity of pyridine increased the electron density of Ni^{2+} salen complex, resulting in the negative shift of the anodic signal. The disappearance of the cathodic signal may be attributed to a direct electron transfer from pyridine to the highly unstable Ni^{3+} to regenerate the more stable Ni^{2+}. The oxidized pyridine, which is a radical cation, may in turn polymerize to generate polymeric materials coating the surface of the electrode. The color of the electrode surface also turned darker during the electrochemical process, supporting the polymerization of the pyridine hypothesis. This coating obstructs further electrochemical reaction at the Ni^{2+} salen complex, resulting in the loss of the signal in the next scan. To solve this problem, we tried to clean the adsorbed polymer on the surface of the modified electrode by using vibrational energy from ultrasonication. The voltammogram of the sonicated electrode showed almost full recovery of the oxidation current (Figure 2). These results suggested that the materials covered the electrode by weak physisorption and simple sonication for 5 min can effectively regenerate a usable electrode for the next measurement.

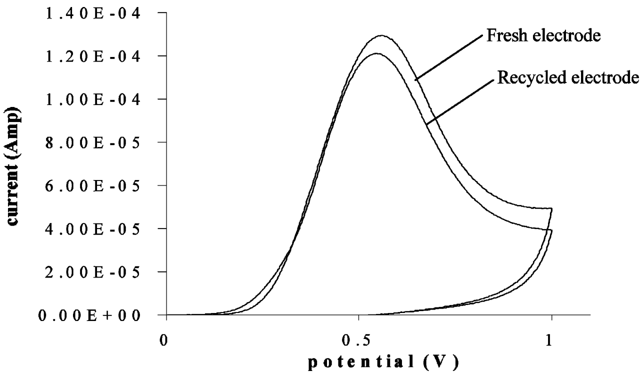

Figure 2. Cyclic voltammogram of a freshly prepared electrode coated with Ni(II)−**polymer 3** complex and the recycled electrode in electrolyte containing 2.48×10^{-1} M pyridine.

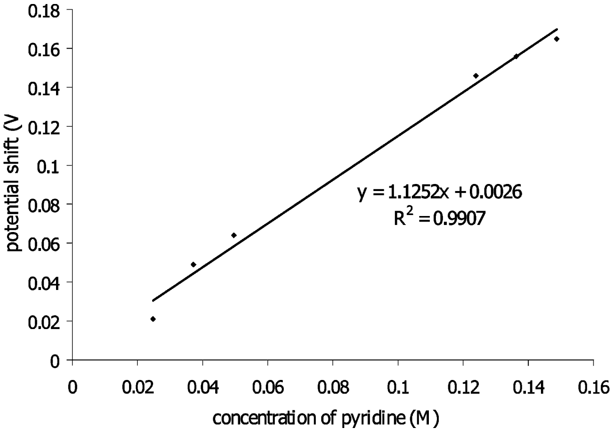

Figure 3. Plot between the potential shift of anodic signal and the concentration of pyridine for the electrode coated with Ni(II)−**polymer 3** complex.

To substantiate that the potential shift of the anodic signal was caused by pyridine, the concentration of pyridine was varied. The potential shift of the anodic peak was linearly correlated to the concentration of pyridine within the range of 2.48×10^{-2} to 1.48×10^{-1} M (Figure 3).

In conclusion, we have shown that both the length of the glycolic chains and the nature of the metal ions play pivotal roles in the solubility of the polymeric metal−salen complexes. Moreover, the preliminary electrochemical study revealed that the soluble polymeric Ni(II)−salen complex can be used conveniently to prepare a modified working electrode for electrochemical sensing of pyridine.

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