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Soluble and Electroactive Nickel Bisdithiolene Complex Polymers

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A Contribution from

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Soluble and Electroactive Nickel Bisdithiolene Complex Polymers

ABSTRACT: A new electroactive and soluble polymer, based on nickel bisdithiolene linkages along the polymer main chain, has been prepared. This polymer, poly[bis-(4-oxystyryldithiolene)nickel] (PBOSD-Ni), can be dissolved in both aqueous and organic solvents in the reduced form. UV-VIS spectra show features typical to comparable nickel bisdithiolene complexes and the $[NiL_2]^{2-} \rightleftarrows [NiL_2]^{1-} \rightleftarrows [NiL_2]^{0}$ oxidation states are observed electrochemically.

Soluble and Electroactive Nickel Bisdithiolene Complex Polymers

Considerable effort has been devoted to the synthesis and understanding of transition metal bisdithiolenes[1] and structurally related complexes[2] which possess interesting electrochemical, optical, magnetic, liquid crystalline,[3] electrically conductive and superconductive[4] properties. A number of polymers and oligomers based on the square planar MS_4 center have also been prepared that are electroactive and conductive. These include poly(metal tetrathiooxalates),[5] poly(metal ethylenetetrathiolates),[6] poly(metal tetrathiosquarates),[7] poly(metal tetrathiafulvalene tetrathiolates),[8,9] poly(metal tetrathianaphthalenes)[10] and poly(metal benzenetetrathiolates).[11] Most of these metal complex polymers are insoluble and infusible solids due to their ribbon like rigid structure. During synthesis some of these systems possess solubility which can be attributed to the high charge density along the polymer backbone, but precipitation to amorphous powders prohibits resolubilization.

We report here on the synthesis and properties of a new metal complex polymer, poly[bis-(4-oxystyryldithiolene)nickel] (PBOSD-Ni) which, in the reduced form, is *aqueous* and *organic* solvent soluble and exhibits electrochemical properties analogous to the transition metal bisdithiolenes.

Bis-(4-styryldithiocarbonate)oxide (BSDTO) was the required monomer precursor for this study. The synthesis of this compound was carried out in three steps as shown in Scheme I. Starting with diphenylether (x=O), Friedel-Crafts acylation with chloroacetyl chloride in the

Insert Scheme I

presence of $AlCl_3$ lead to bis-(4-chloroacetylphenyl)oxide. Bromoacetyl bromide and bromoacetyl chloride were also used as acylating reagents, but low yields of product were obtained. Bis-(4-chloroacetylphenyl)oxide was reacted with the potassium salt of O-ethyl xanthate and the product (1) cyclized by HBr in acetic acid to produce the desired BSDTO dithiocarbonate (2) in an overall

45% yield. Recrystallization from methylene chloride and acetone yields light-yellow platelets [m.p. 146-148°C; IR (KBr) 1736, 1683, 1635, 1597, 1539, 1496, 1253, 871, 833, 775 cm^{-1}; ^1H-NMR (200 MHz) δ 6.77(s,2H), 7.06(m,4H), 7.42(m,4H); ^{13}C-NMR (200 MHz) δ 192.22, 157.31, 134.08, 128.31, 128.00, 119.52, 111.21; Anal. Found (Calcd): C, 53.53 (53.71); H 2.49 (2.50); S, 31.22 (31.86)]. Some of the synthetic steps were carried out by modification of a published procedure.[12]

Polymerization reactions were carried out at 60°C by treating BSDTO with 6 mole equivalents (based on the number of moles BSDTO) of NaOEt in EtOH to form the tetrathiolate, followed by reaction with a stoichiometric amount of $NiBr_2$ overnight as shown in Scheme II. For the first step, the cleavage of the dithiocarbonate to tetraanion, Vicente's results show[6] there are

Insert Scheme II

problems of "half opening" versus "full opening" of a tetrathiapentalene-dione. We carried out a systematic study of the formation conditions of the tetraanion in order to optimize the polymer synthesis. Our results show that the tetraanion is extremely sensitive to oxygen and, when there is even a small amount of oxygen present in the reaction system, an insoluble polymeric by-product forms. Ethoxide cleavage reactions were carried out in scrupulously deoxygenated nitrogen and the methylated derivative formed by reaction with CH_3I. HPLC analysis[13] showed that between 30 and 60 minutes reaction time BSDTO could be quantitatively converted to tetramethylated product and thus complete conversion to the tetraanion was accomplished. The elemental analysis of the tetramethylated species is as expected: Anal. Found (Calcd.): C, 59.26 (59.08); H, 5.63 (5.45); S, 31.15 (31.54).

Complexation polymerization of the tetraanion with Ni(II) in EtOH leads to a dark brown solution having a typical nickel bisdithiolene complex UV-VIS spectrum [λ_{max} (EtOH) 215, 270, 310, 490 and 930 nm].[14] We term this the *reduced* form of the polymer since each metal bisdithiolene site is dianionic and can be represented as $[NiL_2]_n^{-2}$. This form of the polymer is also soluble in H_2O, CH_3CN, CH_3COCH_3 and DMF.

The reduced form of the polymer is air unstable and was oxidized by either O_2 or I_2 to yield a black solid powder (*oxidized* form) which was insoluble in most solvents. The electrical conductivity of a pressed pellet of this form (either oxidant) is $10^{-6}\ \Omega^{-1}\ cm^{-1}$. The oxidized form of the polymer is slightly soluble in DMF with a similar UV-VIS spectrum [λ_{max} (ϵ) (DMF) 265(48,100), 310(54,700), 490(sh. 2,500) and 930(13,200)nm]. The low energy peak at 930 nm is assigned to the $2b_{1u} \rightarrow 3b_{2g}$ transition and is commonly seen at 900 nm in nickel bisdithiolenes.[15] Electron donating substituents are known to shift this peak to slightly lower energies. Though solubility of the oxidized form in DMF is low (*ca.* 10^{-5} M) all of a sample can be made to dissolve.

Elemental analysis results for the iodine oxidized polymer are as expected for the general formula shown in Scheme II except for a somewhat low nickel content. Anal. Found (Calcd.): *C, 47.49 (47.43); H, 2.91 (2.49); S, 33.49 (31.65)*; Ni, 10.80 (14.49); I, 2.17 (0.0); Br, 0.51 (0.0). The high S:Ni ratio of 5.67:1 could be due to ligand based endgroups in short chains or side reactions which yield bisulfide or other non-metal containing linkages. The nickel catalyzed formation of similar thianthrene linkages in poly(nickel benzodithiolene) has been previously postulated.[11] The low halogen content indicates there are very few metal endgroups and the metal bis-dithiolene linkages are essentially in the neutral state.

Cyclic voltammetric analysis shows the reduced form of PBOSD-Ni to be electroactive in solution as shown in Figure 1. Scanning anodically, the polymer undergoes a reversible redox at $E_{1/2} = -0.85$ V corresponding to the $[NiL_2]_n^{2-} \rightleftarrows [NiL_2]_n^{1-}$ reaction and a quasi-reversible redox at $E_{1/2} = +0.09$ V which corresponds to the $[NiL_2]_n^{1-} \rightleftarrows [NiL_2]_n^{0}$ reaction. These peaks correspond well to similar peaks seen for nickel bisdithiolene complexes.[16] All peak currents are linearly dependent on the square root of scan rate demonstrating electron transfer is occurring to solution species. Each cyclic voltammogram shown was carried out on a clean carbon surface due to deposition on the electrode surface during scanning. This phenomenom is presently being investigated in detail.

The optical and electrochemical results indicate that a soluble polymer is formed during the formation of the nickel bisdithiolene units. Our use of the nonconjugated, flexible, diphenyl ether unit in the main chain increases the solubility of this polymer as compared to previously reported MS_4 center containing oligomers and polymers. This new family of polymers is presently being expanded upon in our laboratory by variations of both transition metal ion and ligand type (varied X in Scheme I) and will be reported on further in the near future.

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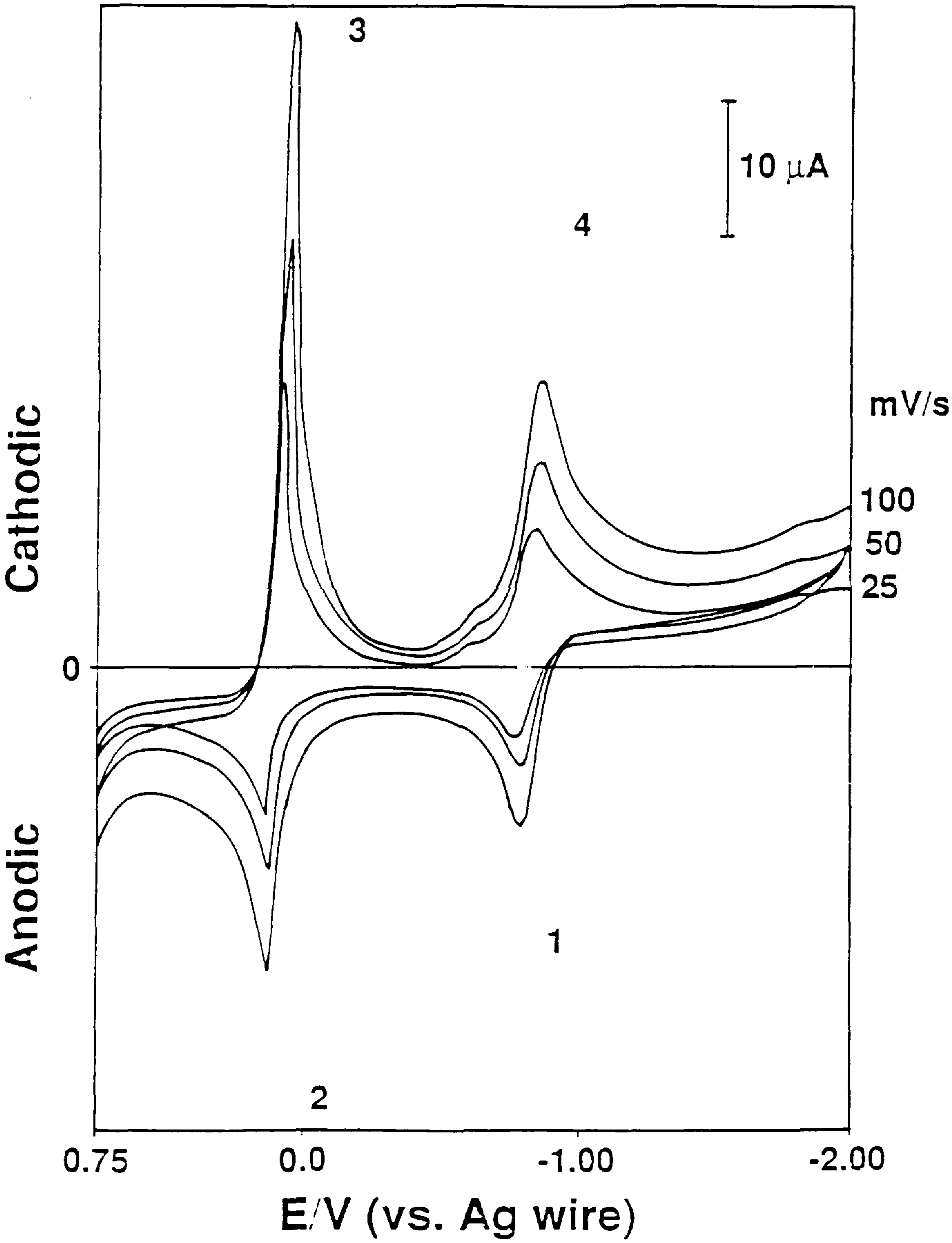
Figure Captions

Figure 1. Cyclic voltammogram for PBOSD-Ni (1.6×10^{-3} M) in DMF, 0.1 M $TBAClO_4$ at carbon working electrode.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10 μA
4
mV/s
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50
25
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Anodic
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2
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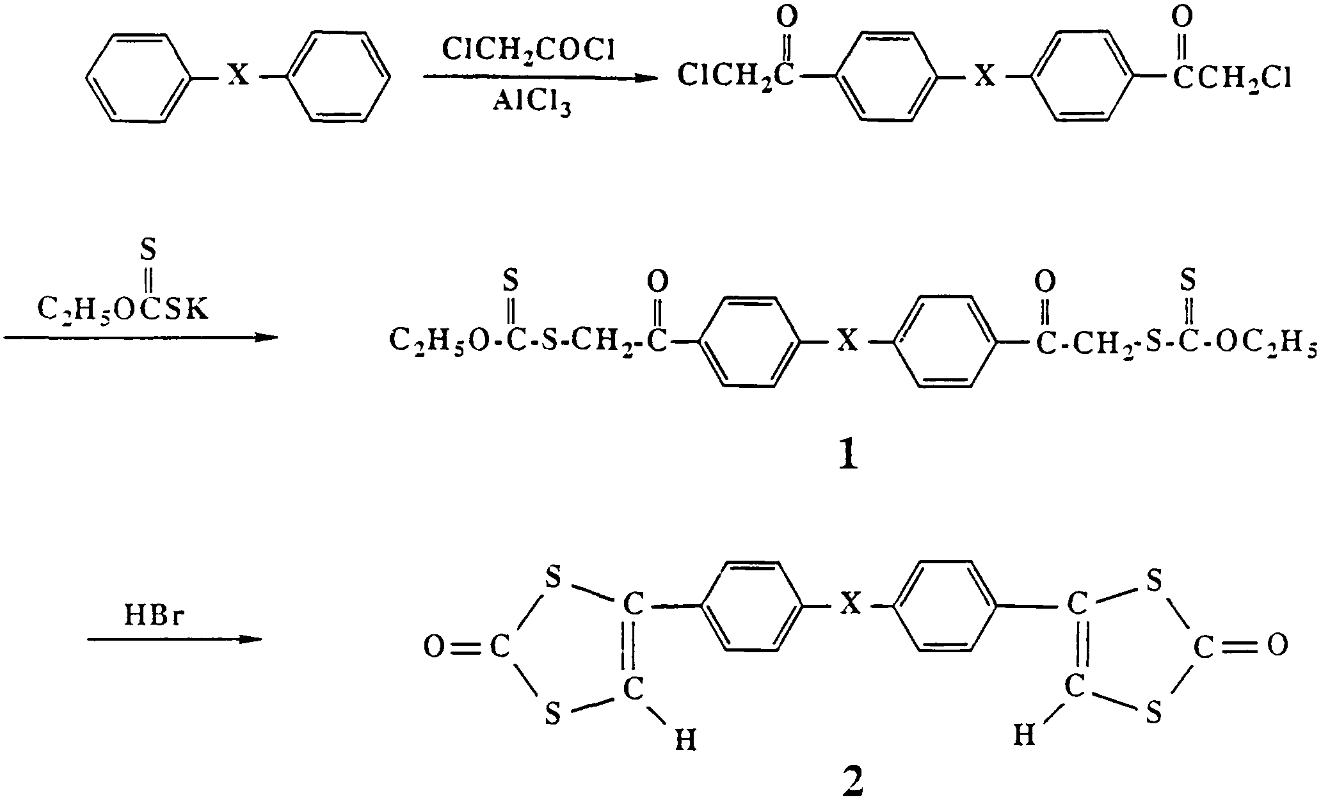
0.0
-1.00
-2.00
E/V (vs. Ag wire)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AlCl3
ClCH2C
CCH2Cl
O
C2H5OCSK
S
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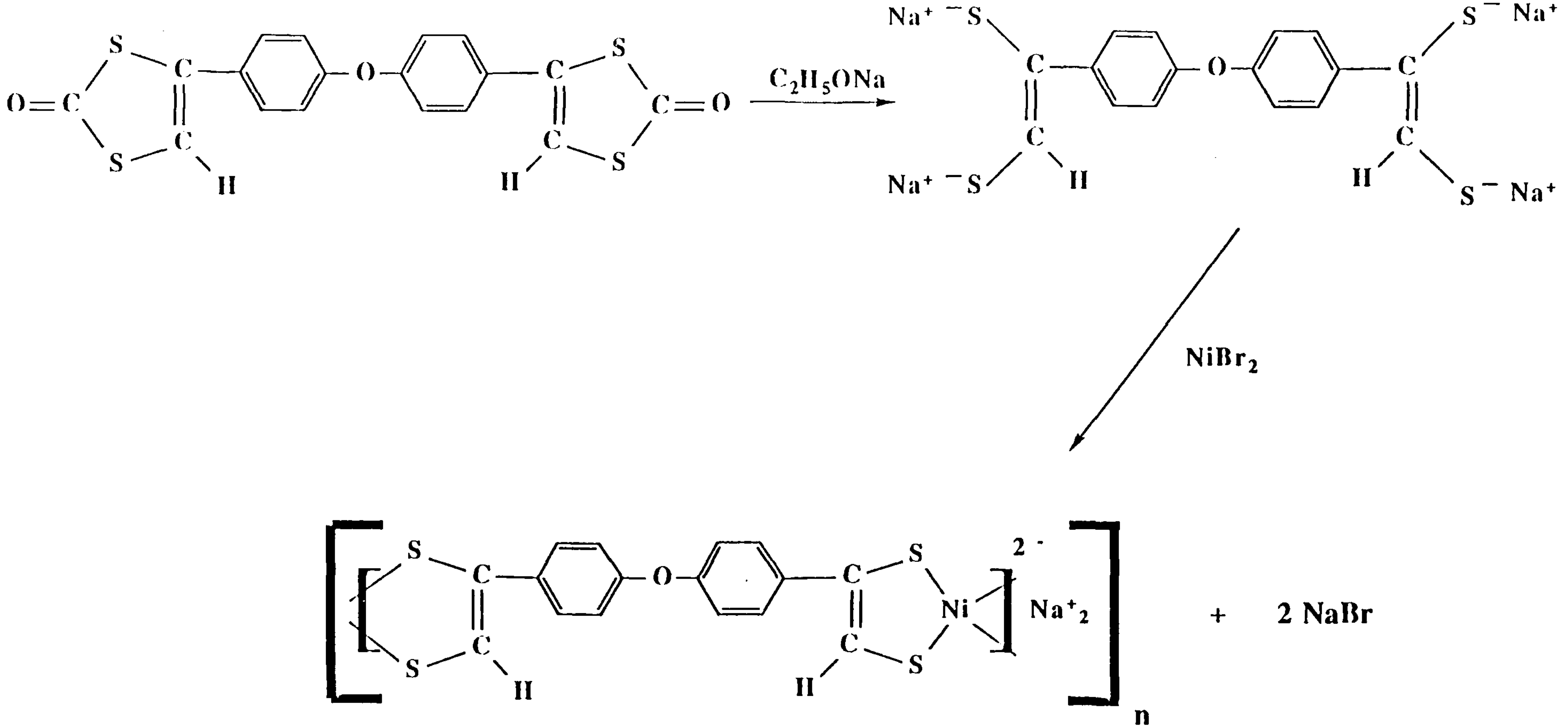
C-CH2-S-C-OC2H5
1
HBr
O=C
C=O
S
C
H
2

Scheme I



Scheme II