in close agreement with the theoretical predictions and previous experimental data on other polymer monolayers. Contrary to an earlier report by Takahashi et al., the chain configuration is not affected by temperature variations in the range 5-30 °C. Consequently, the experimental value of $\nu_\Theta = 0.51$ proposed in ref 26 and 30 cannot be considered as reliable.

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Registry No. PMA, 9003-21-8; PMMA, 9011-14-7.

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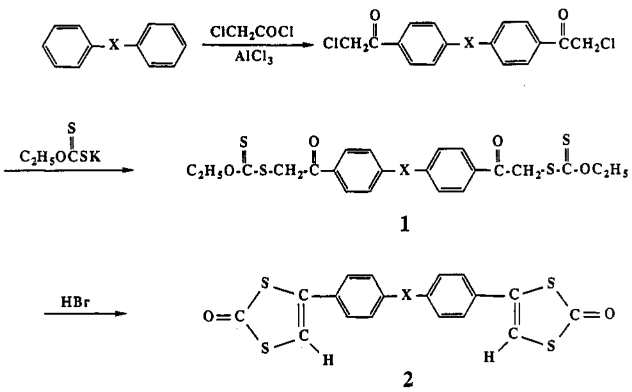
Communications to the Editor

Soluble and Electroactive Nickel Bis(dithiolene) Complex Polymers

Considerable effort has been devoted to the synthesis and understanding of transition-metal bis(dithiolenes)[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 tetrathiafulvalenetetrathiolates),[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 ribbonlike rigid structure. During synthesis some of these systems possess solubility that can be attributed to the high charge density along the polymer backbone, but precipitation to amorphous powders prohibits resolubilization.

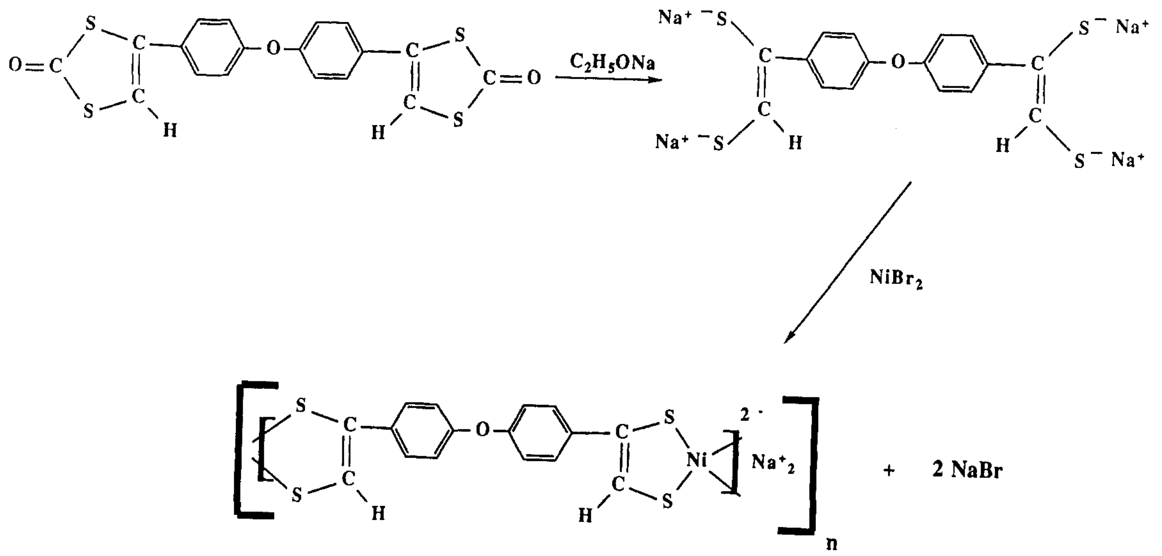
We report here on the synthesis and properties of a new metal complex polymer, poly[[1,1′-oxybis[4-(1,2-dithiolatoethenyl)benzene]]nickel(II)] (PBOSD-Ni) which, in the reduced form, is *aqueous* and *organic* solvent soluble and exhibits electrochemical properties analogous to the transition-metal bis(dithiolenes).

Scheme I



Bis[4-(2-oxo-1,3-dithiolyl)phenyl] 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 diphenyl ether (X = O), Friedel-Crafts acylation with chloroacetyl chloride in the presence of $AlCl_3$ led to bis[4-(chloroacetyl)phenyl] oxide. Bromoacetyl bromide and bromoacetyl chloride were also used as acylating reagents, but low yields of product were obtained. Bis[4-(chloroacetyl)phenyl] oxide was reacted with the potassium salt of *O*-ethyl xanthate

Scheme II



and the product (1) cyclized by HBr in acetic acid to produce the desired dithiocarbonate 2 in an overall 45% yield. Recrystallization from methylene chloride and acetone yields light-yellow platelets [mp 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, 2 H), 7.06 (m, 4 H), 7.42 (m, 4 H); ^{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 mol equiv (based on the number of moles of 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 problems of "half opening" versus "full opening" of a tetrathiapentalenedione. 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 byproduct forms. Ethoxide cleavage reactions were carried out in scrupulously deoxygenated nitrogen, and the methylated derivative was formed by reaction with CH_3I. HPLC analysis[13] showed that between 30- and 60-min 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 bis(dithiolene) 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 bis(dithiolene) site is dianionic and can be represented as $[NiL_2^{2-}]_n$. 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} Ω^{-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, 2500), 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 bis(dithiolene).[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 end groups in short chains or side reactions which yield bisulfide or other nonmetal-containing linkages. The nickel-catalyzed formation of similar thianthrene linkages in poly(nickel benzenetetrathiolate) has been previously postulated.[11] The low halogen content indicates there are very few metal end groups 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 $[NiL_2^{2-}]_n \rightleftarrows [NiL_2^{1-}]_n$ reaction and a quasi-reversible redox at $E_{1/2} = +0.09$ V, which corresponds to the $[NiL_2^{1-}]_n \rightleftarrows [NiL_2^{0}]_n$ reaction. These peaks correspond well to similar peaks seen for nickel bis(dithiolene) 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 phenomenon is presently being investigated in detail.

The optical and electrochemical results indicate that a soluble polymer is formed during the formation of the nickel bis(dithiolene) 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

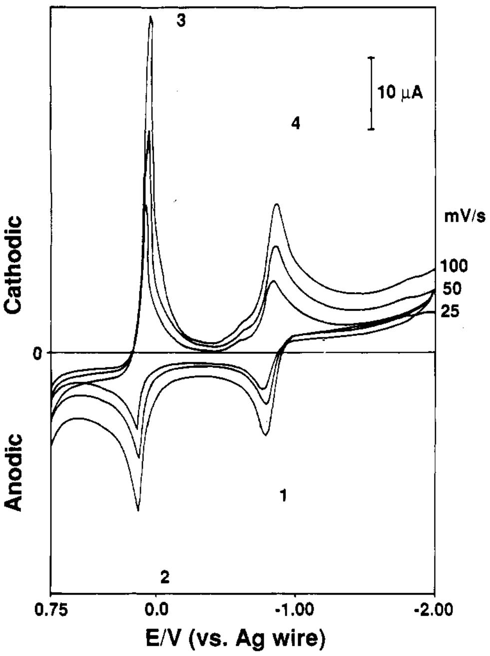


Figure 1. Cyclic voltammogram for PBOSD-Ni (1.6×10^{-3} M) in DMF; 0.1 M $TBAClO_4$ at carbon working electrode.

be reported on further in the near future.

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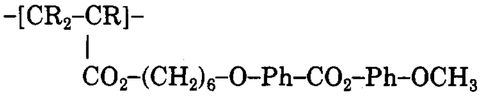
Backbone Conformation of a Mesogenic Side-Chain Polyacrylate

I. Introduction. Small-angle neutron scattering (SANS) is a powerful method for the determination of polymer conformations. It has been extensively used in the melt to access to the backbone conformation of side-chain liquid-crystal polymers by labeling the backbone with deuterium.[1-5] These polymers are different polymethacrylates and polysiloxanes. The nematic phase induces a backbone anisotropy which is always weak and often difficult to determine, but in the smectic phase all SANS experiments conclude that the main chain prefers to orient itself perpendicularly to the mesogenic units and this result may be a general feature. However, recent NMR data about a mesogenic polyacrylate[6,7] seem to indicate that for such a polymer, the backbone is aligned, in the smectic phase, along its mesogenic side chains. Therefore, a small-angle neutron scattering study on the same polymer is of interest. Experimental conditions are specified in section II, and the results are described in section III.

II. Experimental Section. The measure by SANS of the conformation of one polymer backbone in its bulk requires a mixture of similar polyacrylates with hydrogenated and deuteriated backbones.

Both such compounds have been synthetized at the Laboratoire Lêon Brillouin according to a method (already used for the polymers of ref 6, 7) described elsewhere.[8] They have the following formula:



$$-[CR_2-CR]- \\ | \\ CO_2-(CH_2)_6-O-Ph-CO_2-Ph-OCH_3$$

where R = H or R = D.

These polymers have been characterized by gel permeation chromatography and light scattering on line[9] at the Institut Charles Sadron, Strasbourg, as the coupling of both methods gives the absolute molecular weights without reference samples. The molecular weight of the hydrogenated polymer is 27 000 (weight average) and its polydispersity is 2.6 (M_w/M_n); the deuteriated polymer has a molecular weight of 41 000 (weight average) and a polydispersity of 2.0. These molecular weights are about half of those studied by NMR.[6,7]

The polymer has two mesomorphic phases; a nematic phase at higher temperatures and a monolayer smectic phase determined by X-ray[10] and neutron patterns (Figure 1).

The phase-transition temperatures, shown in Table I, were obtained by DSC.

In order to obtain a maximum scattered intensity we have used a sample containing 50% of deuteriated chains.[11] The intensity detected is that scattered by the backbone alone since this is the only part deuteriated. Therefore, the sizes discussed in the following section correspond to those of the main chain without mesogenic.[12] The sample

0024-9297/88/2221-2889$01.50/0