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Electrochemical polymerisation of (2,4,6-trihalophenolato)nickel(II) complexes in solution

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Abstract

The synthesis of bis(2,4,6-trihalophenolato)di/or mono(pyridine)nickel(II) complexes and their characterisation by FT-IR, DSC and elemental analysis were achieved. The polymerisation of these complexes was accomplished in potassium perchlorate solution in *N*,*N*-dimethylformamide by constant potential electrolysis, at room temperature. The structural analysis of the polymers was performed using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques, DSC for the thermal analysis and molecular weight by GPC. The kinetics of the polymerisations were followed by in situ UV–VIS spectroscopy, during the constant potential or constant current electrolysis in two different solvents. The mechanism of the polymerisation was investigated by in situ ESR spectroscopy. There was no induction period for the polymerisation during electrolysis. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bis(2,4,6-trihalophenolato)di(pyridine)nickel(II); Poly(dihalophenylene oxide); Electrochemical polymerisation

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1. Introduction

The original electrochemical polymerisation of a silver salt of 2,4,6-tribromophenol (TBP) in pyridine was achieved by Hunter et al. in 1932 [1]. No characterisation was performed, however, except the colour of the anolyte and the solid poly(dibromophenylene oxide). Later, more detailed studies of electrochemical polymerisation of various phenol derivatives were reported [2–6]. There were also several reports on the electrochemical polymerisation of (2,4,6-trihalophenolate)copper(II) complexes using pyridine, ethylenediamine and tetramethylethylenediamine as neutral ligands, in dimethylformamide and acetonitrile at room temperature, under air or nitrogen [7–20]. However, we can find no record of electrochemical polymerisation of bis(2,4,6-trihalophenolato)nickel(II) complexes in the literature. Recently, the thermal decomposition of one of these complexes in the solid state was published [21]. In the present study, polymerisation of bis(2,4,6-trihalophenolato)di/or mono(pyridine)nickel(II) complexes was attempted by electro-oxidation at the anodic peaks of the voltammograms of the complexes. It was expected, and observed, that electron abstraction should occur from the nickel–oxygen bond to the electrode, and that the radicals produced should polymerise. Moreover, since the molecular weights of electrochemically produced polymers are generally low [7–20], structural analysis by spectroscopic techniques presents few difficulties.

2. Experimental

2.1. Materials

2,4,6-trichlorophenol (TCP), TBP, and 2,4,6-triiodophenol (TIP), (Sigma and Aldrich Chem Co. Ltd.) were used without further purification. The reagent grade pyridine (Py), (Riedel-de Haen AG) was used as a

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neutral ligand. Commercially available nickel sulphate hexahydrate, ($NiSO_4 \cdot 6H_2O$) was used in the preparation of trihalophenolato complexes. *N*,*N*-dimethylformamide (DMF), (Merck) was vacuum distilled over aluminium oxide prior to use. Potassium perchlorate, $KClO_4$, (Riedel-de Haen AG) and tetrabutylammonium tetrafluoroborate, TBATFB, (Aldrich Chem Co.) were used as supporting electrolytes.

2.2. Preparation of nickel complex

2,4,6-trihalophenolato nickel(II) complexes were precipitated from aqueous solutions of reagents. A solution of 0.2 mol NaOH and 0.2 mol trihalophenol with 0.3 mol pyridine in 200 cm^3 distilled water was slowly added to a solution containing 0.1 mol $NiSO_4 \cdot 6H_2O$ in 200 cm^3 distilled water, with vigorous stirring. In all cases blue complexes were recovered by filtration, washed with distilled water, and dried in a vacuum oven to constant weight. The colours of the complexes changed to yellow after drying, most probably due to loss of water of crystallisation. The complexes were characterised by elemental analysis using Leco 932 CHNSO elemental analyser. The elemental analysis and suggested formulae of the complexes are (the experimental errors ±0.3):

	% N	% C	% H
Complex **1** $Ni(TCP)_2$-$Py_2 \cdot 3H_2O$			
Calculated	4.2	39.8	3.0
Found	4.6	39.1	2.7
Complex **2** $Ni(TBP)_2$-$Py_2 \cdot 3H_2O$			
Calculated	3.0	28.4	2.2
Found	2.9	28.6	2.0
Complex **3** $Ni(TIP)_2$-$Py \cdot 3H_2O$			
Calculated	3.0	18.0	1.3
Found	2.7	18.1	1.6

The structural analysis of the nickel complexes was carried out by FT-IR spectroscopy in KBr pellets using a Schimadzu 470 FT-IR spectrometer and UV–VIS spectroscopy in solution using Hewlett Packard 8452 A Diode array model.

2.3. Cyclic voltammetry

Cyclic voltammograms, CV, of the complexes (10^{-1} M) were obtained in TBATBF solution in DMF, CH_3CN and $CHCl_2$, under nitrogen atmosphere, at room temperature. All the CV were recorded at 100 mV/s scan rate. The oxidation, E_a, and reduction, E_c, potentials are;

	Solvent	E_a (V vs Ag/Ag^+)	E_c (V vs Ag/Ag^+)
Complex **1**	DMF	0.10, 0.85	−0.9, −1.5
	CH_3CN	0.75, 1.3, 1.65, 2.0	−0.75, −1.3
	CH_2Cl_2	0.75, 1.25	
Complex **2**	DMF	0.15, 0.80	−0.55, −1.25
	CH_3CN	0.75, 1.05, 1.5, 2.0	−0.50, −1.00, −1.40
	CH_2Cl_2	0.50, 1.00, 1.50	−1.50
Complex **3**	DMF	0.20, 0.75	−0.75, −1.80
	CH_3CN	0.50, 1.10, 1.90, 2.25	−1.40
	CH_2Cl_2	0.70, 1.25, 1.80, 2.00	−0.90, −1.20

Potentioscan Wenking POS 73 potensiostat and Llyod PL3 XY/t recorder were employed for the electrochemical studies.

2.4. Polymer synthesis

Electrochemical polymerisation of bis(2,4,6-trichlorophenolato)di(pyridine)nickel(II), (Complex **1**), bis(2,4,6-tribromophenolato)di(pyridine)nickel(II), (Complex **2**), and bis(2,4,6-triiodophenolato)(pyridine)nickel(II), (Complex **3**) were achieved by using constant potential electrolysis system. The electrolysis were carried out in DMF–$KClO_4$, solvent-supporting electrolyte, using H-type polymerisation cell consisting of 5.0 mm diameter graphite rod as a working electrode and 6 cm^2 stainless steel as a counter electrode. The complexes were electrolysed at 1.0 V under air at different temperatures. Polymers were recovered only from the anode compartment. An insoluble by-product, NiX_2Py_2, was removed by filtration and the polymer was precipitated by addition of ethanol containing a few drops of concentrated HCl. The precipitated polymer was recovered by filtration and dried to constant weight under vacuum. The kinetics of polymerisation were followed by recording the electronic absorption spectrum of the electrolysis solution containing the complex either at 1.0 V or at a predetermined constant current, in a specially designed UV cell [19].

2.5. Polymer characterisation

Fourier-transform infrared analysis: FT-IR spectra were recorded on a Schmadzu 470 model spectrometer with polymers dispersed in KBr discs.

Nuclear magnetic resonance analysis: ^1H-NMR and decoupled ^{13}C-NMR spectra were recorded on a Bruker

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