Coordination Ability of Poly(vinylene-arsine)s towards Transition Metal Ions

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Abstract. Coordinations of poly(vinylene-arsine)s (I) towards transition metal ions were carried out to estimate the coordination ability of phenyl-substituted poly(vinylene-arsine) (1a) and methyl-substituted poly(vinylene-arsine) (1b). No 1a-Co complex was obtained upon addition of an acetone solution of 1a to an acetone solution of cobalt (II) chloride hexahydrate. On the other hand, 1b-Co complexes were obtained in the reactions at different cobalt salt-1b feed ratios. As in the usual case, the bivalent complexes of the reaction run corresponding to the feed ratio of 1:1 [CoCl₂]/[repeating unit of 1b] oxidized readily in air to give very stable complexes of trivalent cobalt. On the other hand, the bivalent complexes of the reaction runs corresponding to the feed ratios of 1:4 and 1:10 both exhibited unusual stability against air oxidation owing to the higher concentration of 1b in the reaction mixture. Reactions of 1 and bis(2,2'-bipyridyl)ruthenium(II) dichloride also provided polymer complexes. In all the cases, 1b had higher coordination property than 1a due to its lower steric hindrance.

1. Introduction

The introduction of transition metal complexes into conjugated polymer backbones provide new dimensions of novel materials with improved electrical, magnetic and catalytic properties. Moreover, the polymer metal complexes offer advantages like recovering from reaction mixtures by simple filtration or reprecipitation, and easy recycling. A variety of transition metal polymer complexes have been synthesized, in which the metal complexes are linked to the backbones as isolated pendants, or are inserted into the polymer backbones.

Poly(vinylene-arsine)s (I) are expected to form polymer complexes with various kinds of transition metals due to the lone pair on the arsenic atom. Because I have arsenic atoms in the backbone, the transition metal can coordinate directly towards its backbone, and the connection of transition metals can be expected. In some reports, organoarsenic compounds have been reported to be superior ligands [1-4]. For example, osmium complexes with the arsenic ligands exhibited phosphorescence with greater quantum yields. However, only one polymer complex coordinated with arsine has been reported [5]. The reason for this is originally difficult synthesis of organoarsenic compounds due to the toxicity of the arsenic sources (arsenic chloride or arsenic hydride, for example). As shown in the previous works, poly(vinylene-arsine)s (1) have been synthesized by ring-collapsed radical alternating...
copolimerization (RCRAC) of phenylacetylene with hexaphenyldicyclohexaarsine \((\text{cyclo}-(\text{PhAs})_6)\) or pentamethylcyclopentaarsine \((\text{cyclo}-(\text{MeAs})_5)\), which is the first soluble polymers containing arsenic atoms in the main chain (Scheme 1) \([6,7]\). In this paper, the coordination abilities of poly(vinylene-arsine)s \((1)\) towards Co ions and Ru ions are estimated.

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\text{cyclo-}(\text{RAs})_n + \text{Ph} \xrightleftharpoons{\text{AIBN}} \text{benzene reflux} \rightarrow \text{CH} = \text{C} \quad \text{Ph} \quad \text{As} \quad \text{R} \quad (\text{n})
\]

**Scheme 1.** Preparation of poly(vinylene-arsine)s \((1)\).

2. Experimental

2.1. Materials
Unless otherwise noted, all reagents and chemicals were purchased and used without further purification. Hexaphenyldicyclohexaarsine \((\text{cyclo}-(\text{PhAs})_6)\) \([8]\) and pentamethylcyclopentaarsine \((\text{cyclo}-(\text{MeAs})_5)\) \([9]\) were prepared according to literature procedures. Phenylacetylene was distilled under reduced pressure. Poly(vinylene-arsine)s \((1)\) were prepared by the method mentioned in other reports \([6,7]\).

2.2. Instruments
All reactions were carried out under an argon atmosphere using Schlenk techniques. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using CHCl₃ as an eluent after calibration with standard polystyrene. \(^1H\) and \(^13C\) NMR spectrum was obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in CDCl₃ or CD₃CN and were referenced to SiMe₄ (TMS). UV-vis spectra were measured on a JASCO V-530 spectrometer, and the samples were analyzed in CHCl₃ at room temperature and on a Perkin Elmer Lambda 19 spectrometer for powder samples analyzed at room temperature. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin Elmer 2000 spectrometer. Cyclic voltammetry analysis was done with a BAS CV-50W Electrochemical Analyzer in a CH₂Cl₂ solution of 0.1M \([\text{CH}_3\text{(CH}_2)_3]_4\text{N-PF}_6\) as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurement.

2.3. Preparation of Poly(vinylene-arsine)s-Cobalt Complex.
Cobalt chloride hexahydrate (12 mg) in acetone (2 ml) was treated with \(1b\) (10 mg) in acetone (4 ml) (Run 6). The reaction mixture was stirred at room temperature for 1 d, heated on the oil-bath under reflux condition for 30 min, and then cooled. The yellow-green complex was isolated by filtration, and then well washed with hexane and acetone. The complex was finally dried under vacuum (product weight = 9 mg). On the other hand, the solvent was removed from the filtrate under reduced pressure and the residue consisting of the uncoordinated cobalt ions and \(1b\)-Co complex was collected. H₂O (25 ml) was then used to dissolve the uncoordinated cobalt ions and isolate them from \(1b\)-Co complex. This uncoordinated cobalt solution (aq.) was used in the determination of the amount of uncoordinated Co ions by EDTA titration (the detailed procedure is presented below).

2.4. Determination of Uncoordinated Cobalt Ions in Aqueous Solution: Direct Titration Using Xylenol Orange Indicator
The uncoordinated cobalt aqueous solution (25 ml) was pipetted into a 500 ml conical flask and diluted with de-ionized water to about 150 ml. The pH was then adjusted to about 6 by the cautious addition of hexamine (pH meter was used). Then, 30 mg of the Xylenol Orange/H₂O solution was added and then titrated with standard 0.01M-EDTA solution until the purple colour started to fade.
From this point, the titrant was added slowly until the end-point was reached and the indicator
turned yellow (1 mole EDTA = 1 mole Co$^{2+}$) [10].

2.5. Preparation of Poly(vinylene-arsine)-Ruthenium Complex.
A typical experimental procedure is as follows. A half equimolar amount (vs vinylene-arsine structure) of cis-(bpy)$_2$RuCl$_2$·2H$_2$O and poly(vinylene-arsine) were stirred in a refluxing deaerated CHCl$_3$ / ethanol (1/1) for 24 h. The solvent of the resulting mixture was reduced by evaporation and the
resulting solution was poured into methanol solution of NH$_4$PF$_6$. After reprecipitation several times,
the polymer complex was obtained as a pink-orange powder (2).

3. Results and Discussion

3.1. Poly(vinylene-arsine)-Cobalt Complex
Poly(vinylene-arsine)-cobalt complexes have been prepared and studied because the coordination of
the compounds of tertiary arsines with cobalt has been well studied providing background information
for this research [11-14].

| Table 1. Results of polymerization |
|-----------------------------------|
| run | Feed ratio | Reaction condition | 1b-Co complex | Colour of the complex |
|-----|------------|--------------------|--------------|---------------------|
| 1   | 1:20       | acetone 200 ml     | 79           | Blue-green          |
| 2   | 1:10       | acetone 100 ml     | 42           | Blue-green          |
| 3   | 1:1        | acetone 10 ml      | 4            | Yellow-green        |
| 4   | 1:10       | acetone 100 ml     | 37           | Blue-green          |
| 5   | 1:4        | acetone 40 ml      | 28           | Sky blue            |
| 6   | 1:1        | acetone 10 ml      | 9            | Yellow-green        |

**Scheme 2.** Preparation of cobalt–complex (1-Co).

Polymer metal complexes were prepared by adding an acetone solution of 1a or 1b to an acetone
solution of cobalt chloride hexahydrate at different feed ratios. The reaction mixtures were stirred for 1
day at room temperature, refluxed for 30 min, and then, cooled. No 1a-Co complex was obtained due
to the bulky structure (phenyl group) of 1a. On the other hand, 1b-Co complexes precipitated even
before refluxing (Scheme 2). The products were isolated by filtration. The residue was then washed with n-hexane and acetone, and finally, dried under vacuum. The results are summarized in Table 1.

The 1b-cobalt complexes exhibit different colors. The color of the complex is some guide to the stereochemistry. Mellor and Craig reported that square complexes of bivalent cobalt were some shade of brown while the ionic or tetrahedral complexes varied in color from pink or mauve to blue. In this case, the blue-green complexes of run 1 corresponding to the feed ratio of 1:20 [CoCl₂]/[repeating unit of 1b] and runs 2 and 4 corresponding to the feed ratio of 1:10, and the sky-blue complexes of run 5 corresponding to the feed ratio of 1:4 suggest complexes of bivalent cobalt.

Moist cobalt(II) chloride becomes green on the surface in air, owing to oxidation, and bivalent complexes are oxidized readily in air to give very stable complexes of trivalent cobalt. When air is admitted to the reaction mixture, oxidation takes place rapidly and the cobalt(II) salt dissolves to give a green solution from which a green complex of trivalent cobalt was obtained on cooling [14]. This explains the yellow-green complexes of runs 3 and 6 corresponding to the feed ratio of 1:1. Apparently, the bivalent complexes of runs 3 and 6 were sensitive to oxidation by air due to the lower polymer concentration in the reaction mixture.

It has been established that the colors of the 1b-Co complexes which serve as some guide to the stereochemistry of the complexes and valency of the coordinated cobalt could be controlled by the feed ratio of cobalt(II) chloride hexahydrate and 1b. This is the particularly interesting result since it may mean controlling the chemical and physical properties of the complexes for specific applications.

Cobalt(II) chloride formed stable, slightly soluble complexes with 1b. The complexes of runs 4, 5, and 6 corresponding to the feed ratios of 1:10, 1:4, and 1:1 were analyzed by FTIR and were observed by their colors before and after washing with n-hexane and acetone to investigate their stability against oxidation. No changes were observed in the IR spectra and in the colors of the complexes before and after washing showing that the complexes are indeed stable. The cobalt salt was insoluble in chloroform and 1b was soluble. While the obtained polymer metal complexes of runs 1 and 4 are soluble and those of run 6 and of the other runs are slightly soluble in the same solvent. All the obtained complexes are only either slightly soluble or insoluble in other solvents such as DMF, DMSO, benzene, acetone, and THF, which dissolves polymer 1b.

To estimate the Co ion content in the polymer metal complex, the amount of uncoordinated Co ions was determined by EDTA titration. The molar ratios of Co ion and repeating unit of 1b in the polymer metal complexes of runs 4, 5, and 6 are 1:7, 1:3, and 1:1, respectively. Complexes of runs 4 and 5 corresponding to the feed ratio of 1:10 and 1:4, respectively, are expected to be complexes of bivalent cobalt as exhibited by their colors. The reluctance of the bivalent cobalt to form octahedral complexes with covalent bonds is well known [14]. This is consistent with the estimated molar ratios of Co ion and repeating unit of 1b in the polymer metal complexes of runs 4 and 5. For run 6, the estimated molar ratio of Co ion and repeating unit of 1b in the polymer metal complex is reasonable owing to the steric hindrance involved in the coordination of the polymer towards the metal ion.

**Figure 2.** UV-vis absorption spectra of (a) poly(vinylene-arsine)-cobalt complexes of run 6 (1:1 [CoCl₂]/[repeating unit of 1b] feed ratio) in powder, (b) poly(vinylene-arsine)-cobalt complexes of run 4 (1:10 feed ratio) in powder.
The UV-vis spectrum of the complex of run 6, which corresponds to the feed ratio of 1:1, showed a metal-to-ligand charge transfer (MLCT) at 370 nm (Figure 2a). This absorption suggests that the bivalent complexes of this reaction run oxidized in air to give very stable complexes of trivalent cobalt. On the other hand, no MLCT is observed in the UV-vis spectra of the complexes of run 4, which corresponds to the feed ratio of 1:10 (Figure 2b) and of the complexes of run 1, which corresponds to the feed ratio of 1:20, in chloroform showing that the bivalent complexes of these reaction runs exhibit unusual stability against air oxidation owing to the higher concentration of 1b in the reaction mixture.

3.2. Poly(vinylene-arsine)- Ruthenium Complex

Complexations of the poly(vinylene-arsine)s with ruthenium ions were carried out (Scheme 3). Half equimolar amount (vs vinylene-arsine structure) of cis-(bpy)2RuCl2·2H2O and the poly(vinylene-arsine) are stirred in a refluxing deaerated CHCl3 / ethanol (1/1). The solvent of the resulting mixture was reduced by evaporation and the resulting solution was poured into methanol solution of NH4PF6 to yield the polymer complex. The polymer was purified by repeating the reprecipitation. In the case of phenyl-substituted poly(vinylene-arsine) (1a), the obtained polymer complex (2a) was little colorized, which suggests little amount of Ru ions. On the other hand, the complexation of methyl-substituted poly(vinylene-arsine) (1b) resulted in red solid (2b). The obtained polymer 2b was soluble in CH2Cl2 and acetonitrile, and insoluble in benzene. The 1H NMR spectrum of 2b showed the peaks assignable to the bipyridyl group. The new peaks of the methyl protons (a’) appeared at δ 0.3 ppm – 0.8 ppm, which are derived from the coordination of ruthenium ions. The integral ratio of the peak attributed to the aromatic and vinyl protons and the peak of the methyl protons was 8.94 : 3 and that of the peak (a’) and the sum of the methyl peaks was 0.58 : 3. The estimations from these ratio suggested that 18.3% and 19.4% of arsines were coordinated with ruthenium ions, respectively. On the other hand, there was little difference in the 1H NMR spectra of 2a and 1a, which suggests no or little complexation with ruthenium ions.

The UV-vis absorption spectra of 2a and 2b showed an absorption peak at around 470 nm, which is derived from metal-to-ligand (bpy) charge transfer (MLCT) as well as an strong absorption due to the aromatic groups in the UV region. This result also indicates the incorporation of the complexes. Cyclic voltammetry (CV) measurement of 2a in CH2Cl2 showed a reversible oxidation peak derived from the oxidation of Ru(II) ions. The potential difference between the oxidation peak and the half oxidation peak was 40 mV, which suggests little interaction between Ru ions when around 20% of arsine is coordinated to Ru ions.

4. Conclusions

The coordination ability the poly(vinylene-arsine)s towards Co ions and Ru ions in acetone were described. The poly(vinylene-arsine) derived from hexaphenylcyclohexaarsine (1a) formed no cobalt complex upon addition of an acetone solution of the polymer to an acetone solution of cobalt(II) chloride hexahydrate due to its bulky structure. On the other hand, the poly(vinylene-arsine) derived
from pentamethylcyclopentaarsine (1b) formed the 1b-Co complexes at different cobalt salt-polymer ratios due to its less bulky structure. As in the usual case, the bivalent complexes of the reaction run corresponding to the feed ratio of 1:1 [CoCl₂]/[repeating unit of 1b] oxidized readily in air to give very stable complexes of trivalent cobalt. On the other hand, the bivalent complexes of the reaction runs corresponding to the feed ratios of 1:10 and 1:4 both exhibited unusual stability against air oxidation owing to the higher concentration of the polymer in the reaction mixture. The complexations of the poly(vinylene-arsine)s with ruthenium ions were carried out to result in the lower coordination ability of 1a. The obtained polymer complex showed the absorption peak derived from the incorporated ruthenium complex. The polymer also exhibited a reversible oxidation peak of Ru ion.

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