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Syntheses of Bipyridine-containing Polyamides and their Metallation with Ruthenium Ions*

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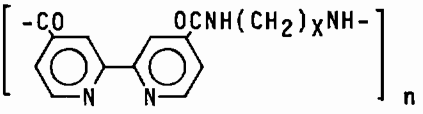
Abstract

The polyamides, [–CO(C_5H_5N·C_5H_3N)CO·NH-(CH_2)$_x$NH–]$_n$ (x = 2 or 6), that incorporate 2,2′-bipyridine groups in the main chains have been synthesized by a homogeneous polycondensation between *p*-nitrophenyl 2,2′-bipyridine-4,4′-dicarboxylate and diamines. The metallation of the preformed polyamides with *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O has been studied by electronic spectroscopy. In the polymers reacted with the Ru compound, each Ru ion is coordinated to one nitrogen atom from a bipyridine group in the polyamides: the bipyridine groups of the polyamides take the *cis* form due to a strong steric effect.

Introduction

The polymers that incorporate ruthenium(II) chelates attract special interest from the viewpoints of electrochemical and/or photochemical reactions [1–3]. The syntheses of metal chelate polymers, therefore, have been attempted by metallation of preformed ligand-containing polymers such as poly(vinylpyridine) and vinylbipyridine–styrene copolymers [2]. The disadvantage of this method is that the metallation is difficult to complete for steric and/or electrostatic reasons. An important approach to solve this problem has been given by the electrochemical polymerization of vinyl-substituted metal-chelate monomers such as [Ru(bpy)$_2$(vpy)]$^{2+}$ (bpy = 2,2′-bipyridine; vpy = 4-vinyl-4′-methyl-2,2′-bipyridine) [3]. In this method, however, the metal–chelate polymers were obtained as a thin film supported on the electrode. It is still important, therefore, to study the metallation of chelating polymers with a high coordination capacity. As a part of this work, we have synthesized the new polyamides **1** and **2** that incorporate bpy groups in the main chains. The metallation of the polyamides with *cis*-bis(bpy)ruthenium(II) ions has also been studied.

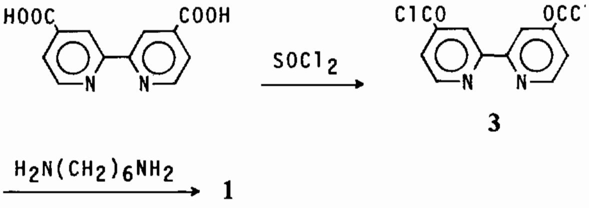


1, X = 6; **2**, X = 2

Results and Discussion

Syntheses of Bipyridine-containing Polyamides

The synthesis of the polyamide **1** was attempted initially by the following interfacial reaction (Scheme 1) that had been commonly employed for the syntheses of polyamides [4]. The second reaction step in the scheme was performed by adding dropwisely a dichloromethane solution of 2,2′-bipyridine-4,4′-dicarboxylic acid chloride (**3**) to an aqueous solution contianing 1,6-hexamethylenediamine (HMDA) and NaOH. A polycondensation reaction occurred immediately on interface between the organic and the aqueous layers. The product exhibited IR bands characteristic of polyamides: 3290 m^{-1} (assignable



Scheme 1.

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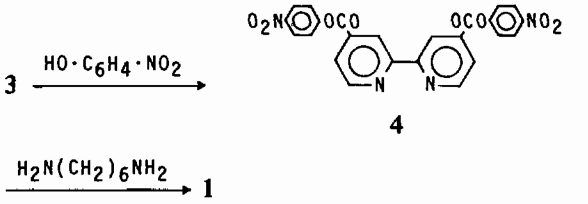
to NH stretch), 1640 cm^{-1} (amide I band), 1530 (cm^{-1} (amide II band), and 1295 cm^{-1} (amide III band). In addition to these intrinsic bands, a weak band was observed at 1725 cm^{-1}. This band could be assigned to the C=O stretch of the carboxylic acid that was formed by the hydrolysis of the acid chloride used as the starting material; the polyamide involved the acid probably at the chain ends. Therefore, we have developed the following polycondensation between the ester (4) and diamines in a homogeneous system (Scheme 2). The product of this reaction exhibited broad IR bands characteristic of polyamides (the IR data are collected in 'Experimental'). No IR band was observed in the range 1700–1780 cm^{-1} where acid C=O stretching bands might appear, and the NO_2 bands (1340 and 1520 cm^{-1}) of 4 were not found in the spectrum. These IR data indicated that the polyamide 1 was obtained with a high purity. The inherent viscosity η_{inh} was as high as 0.62 in hexamethylphosphoramide (HMPA) solution. The product was insoluble in common organic solvents; it was soluble in formic acid and slightly soluble in HMPA. This low solubility is also one of the features of polyamides.

When ethylenediamine (EDA) was used in place of HMDA, the polyamide 2 was obtained; it was characterized by the IR spectrum.



Scheme 2.

Metallation

A formic acid solution containing the preformed polyamide 1 and *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ showed the same solution electronic spectrum as that of the ruthenium compound in formic acid. The nitrogen atoms of the bpy groups in the polyamide were protonated in formic acid so strongly that the ruthenium ions could not be coordinated to the nitrogen atoms of the polyamide.

When the fine powder of 1 was refluxed in an aqueous solution of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$, the resulting solution exhibited an electronic spectrum differing from the rutehnium compound as shown in Fig. 1, although a part of the sample powder remained without being dissolved into the solution. A band assignable to metal-ligand charge transfer (MLCT band) was displaced to a shorter wavelength by *ca.* 8 nm from the corresponding band of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ in aqueous solution. The same spectrum change was observed for an aqueous *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ solution treated with polyamide powder for a week at room temperature. These observations suggested that the ruthenium ions were coordinated to the polyamide to form a water-soluble polymer complex. Essentially the same phenomena were observed for the reaction between the polyamide 2 and the ruthenium compound.

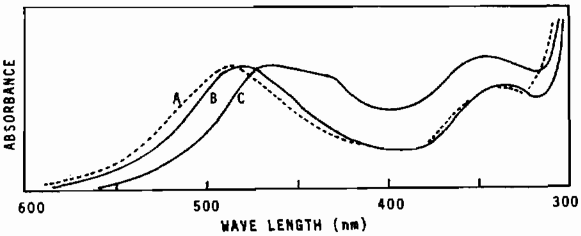


Fig. 1. Electronic spectra of aqueous solutions of (A) $Ru(bpy)_2Cl_2 \cdot 2H_2O$, (B) $Ru(bpy)_2$–polyamide complex, (C) a mixture of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ and excess isonicotinic acid. An aqueous solution containing $Ru(bpy)_2Cl_2 \cdot 2H_2O$ and isonicotinic acid in the mole ratio 1:1 exhibited an MLCT band at 470 nm, and the band shape resembled that of the spectrum B.

Three types of coordinations are conceivable for the $Ru(bpy)_2$–polyamide complex: (a) only one ruthenium coordination site is occupied by a nitrogen atom from the polyamide, (b) two sites are occupied by two nitrogen atoms from different bpy groups of the polyamide, and (c) a bpy group of the polyamide forms a chelate ring with a ruthenium ion. The coordination type of the polymer complex has been characterized by comparing the observed electronic spectra with those of monomeric analogues. An aqueous solution of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ exhibited an MLCT band at 488 nm (Fig. 1). This wave length was different from the value *ca.* 550 nm of $[Ru(bpy)_2Cl_2]$ solution spectra in common organic solvents, and was almost the same as that reported for $[Ru(bpy)_2(H_2O)_2]^{2+}$ [5]. Probably, the chloride ions of $[Ru(bpy)_2Cl_2]$ are substituted with water molecules in aqueous solution. An aqueous solution containing *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and isonicotinic acid (abbreviated as ina) in the mole ratio 1:1 showed a band at 470 nm with a weak hump at *ca.* 440 nm, whereas an aqueous solution of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and excess ina (ina/Ru > 2) exhibited a band at 464 nm with a shoulder at *ca.* 430 nm (Fig. 1). The former spectrum is attributable to $[Ru(bpy)_2(ina)(H_2O)]^{2+}$ and the latter to $[Ru(bpy)_2(ina)_2]^{2+}$, because these spectra respectively resemble those of $[Ru(bpy)_2(py)X]$ and $[Ru(bpy)_2(py)_2]$ (py = pyridine; X = inorganic ligand) in non-aqueous solvents [6, 7]. The electronic spectra of the $Ru(bpy)_2$–polyamide complexes exhibited a band at 480 nm, and the band shape closely resembled that of $[Ru(bpy)_2(ina)(H_2O)]^{2+}$ (Fig. 1). Accordingly, the polymer complexes involve the coordination type A with a weak Ru–N bond.

The chelate ring of the coordination type C is not formed in the polymer complexes; this type of coordination should result in a band at *ca.* 450 nm where $[Ru(bpy)_3]^{2+}$ exhibits an MLCT band [8]. The bpy groups of the polyamides are thought to be in an equilibrium between the *cis* and the *trans* forms, the latter being predominant due to a steric effect. The chelate effect is not strong enough to stabilize the *cis* form in the $Ru(bpy)_2$–polyamide complexes: only one site of ruthenium is occupied by a nitrogen atom of the polyamide that is in the *cis* form.

Experimental

Preparation of p-Nitrophenyl 2,2'-Bipyridine-4,4'-dicarboxylate 4

2,2'-Bipyridine-4,4'-dicarboxylic acid (4.09 mmol) was refluxed with thionyl chloride (50 ml) for *ca.* 20 h. Excess thionyl chloride was removed by distillation and then the residue was dried in vacuum. To the acid chloride (3) thus obtained were added *p*-nitrophenol (9.9 mmol) and triethylamine (10 mmol) in dry tetrahydrofuran (35 ml). A fine powder was formed immediately. After the mixture was heated at 60 °C with stirring for 3 h, the product was suspended in 50 ml of water, filtered off, and dried in vacuum. Recrystallization from 1,4-dioxane yielded colorless fine needles. Yield: 62%; melting point (m.p.): 285–290 °C. IR spectrum (KBr): 1740 (C=O stretch of ester), 1625 and 1580 (aromatic ring deformation), 1520 (asym. NO_2 stretch), 1340 cm^{-1} (sym. NO_2 stretch). *Anal.* Calc. for $C_{24}H_{14}N_4O_8$: C, 59.26; H, 2.90; N, 11.52. Found: C, 59.03; H, 3.00; N, 11.37%.

Polycondensation of 4 with Diamines

93.4 mg (0.80 mmol) of 1,6-hexanediamine was dissolved in 3 ml of HMPA, which was purified by distillation at 82–83 °C under a reduced pressure of 3 mmHg before use. To the solution was added 391 mg (0.80 mmol) of 4 little by little under a nitrogen atmosphere. The resulting mixture was heated at 60 °C for *ca.* 20 h with stirring. The obtained viscous solution was cooled and then poured dropwisely into methanol (40 ml). After the mixture was stirred at 40–45 °C for 0.5 h, the product was separated by filtration, washed with a large amount of methanol at 40–45 °C, and dried in vacuum for 1 h. Yield: 60%; m.p.: >300 °C. IR spectrum (KBr): 3280 (NH stretch of amide), 3060 (aromatic CH stretch), 2915 and 2850 (CH stretch of $-CH_2-$), 1635 (amide I band), 1595sh (aromatic ring deformation), 1530 (amide II band), 1300 cm^{-1} (amide III band); UV spectrum (formic acid solution): 319 (2×10^4) and 256 nm (1.4×10^4); η_{inh} (HMPA solution): 0.62. *Anal.* Calc. for $C_{18}H_{20}N_4O_2 \cdot H_2O$: C, 63.14; H, 6.48; N, 16.36. Found: C, 62.79; H, 6.64; N, 16.52%.

The polycondensation of 4 with ethylenediamine was performed by essentially the same method as described above. Yield: 72%; m.p.: >300 °C. IR spectrum (KBr): 3270 (NH stretch), 3060 (aromatic CH stretch), 2920 and 2840 (CH stretch of $-CH_2-$), 1640 (amide I band), 1590sh (aromatic ring deformation), 1525 (amide II band), 1295 cm^{-1} (amide III band); UV spectrum (formic acid solution): 319 (2×10^4) and 255 nm (1.5×10^4); η_{inh} (HMPA solution): 0.78. *Anal.* Calc. for $C_{14}H_{12}N_4O_2 \cdot 1.5H_2O$: C, 56.94; H, 5.12; N, 18.97. Found: C, 56.95; H, 5.13; N, 19.89%.

Metallation

The metallation of the polyamides was carried out by refluxing 6 mg of 1 in an aqueous solution of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (9 mg/5 ml) for *ca.* 5 h, or alternatively by stirring an aqueous solution of the two materials mixed in the same ratio as described above for 7 days at room temperature. A small part of each resulting solution was taken out, and was diluted with water so that the solution concentration was adequate for the electronic spectrum measurements. The spectra were confirmed to be unchanged by further reaction. The solution spectrum was recorded by the use of a Varian DMS-80 VL-UV spectrophotometer. *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ supplied from Alfa was used without further purification.

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