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# Thermal analysis, Raman spectroscopy and scanning electron microscopy of new polymeric material containing in-chain ruthenium complex: Poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene} and poly-{*trans*-[$RuCl_2(vpy)_4$]-4 vinylpyridine-styrene}

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## Abstract

This work reports the preparation and characterization of the binary copolymer poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene} and the terpolymer poly-{*trans*-[$RuCl_2(vpy)_4$]-4 vinylpyridine-styrene}, obtained through the chemical reaction between *trans*-[$RuCl_2(vpy)_4$] (vpy is 4-vinylpyridine), 4-vinylpyridine and styrene (ST) using benzoyl peroxide. The synthesis was controlled by thin layer chromatography (TLC) and by monitoring the viscosity of the reaction medium. The resulting copolymers are characterized by means of UV–vis. spectroscopy, thermal analysis, Raman spectroscopy and scanning electron microscopy (SEM). The thermal properties of the copolymer were reported by differential scanning calorimetry (DSC), thermogravimetric and differential thermal analysis (TG/DTA) and dynamic–thermal–mechanical analysis (DTMA). Raman spectroscopy results showed that the polymerization takes place from both the vinyl group of the metal complex monomer and the vinyl group of the vinyl monomer, demonstrating the complex incorporation in the polymer matrix. Additionally, the Raman results showed that the redox polymer structure of the copolymer is very similar to that of the monomer. The properties of both materials are discussed.
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*Keywords:* Copolymer; Terpolymer; Ruthenium complex; Metal polymer

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## 1. Introduction

Electroactive transition metal ions may be incorporated into polymeric films by using, for example, electrostatically bound Nafion or protonated PVP through ion-exchange, or using covalently bound redox polymers (e.g. metal complexes coordinated to polyvinylpyridine, PVP) yielding in both cases pendant transition metal complex polymers. In the latter, the polymer electroactive transition metal may be incorporated through two main processes. In polymers containing functional groups capable of acting as ligands, e.g. metallopolymer derivatives of poly(4-vinyl)pyridine, their ability to coordinate metal ions is due to the presence of pyridine N atoms resulting from a direct synthesis of the polymer containing a metal complex [1,2]. Polymers based on the application of coordination forces have been prepared in a few cases only. The first direct synthesis of a polymer containing a transition metal complex gave rise to a coordination polymer based on mixed ruthenium(II)-terpyridine complexes and was described recently in the literature [3,4]. More recently Heller and Schubert [5], describe the utilization of a new functional monomer, containing a styrene substituent at one ligand and a hydroxymethyl functionality at the other ligand of the octahedral transition metal complex leading to a well-defined supramolecular polymer. The combination of inorganic transition metal complex and a polymeric structure leads to new materials with interesting physical and chemical properties. In this paper we describe an alternative

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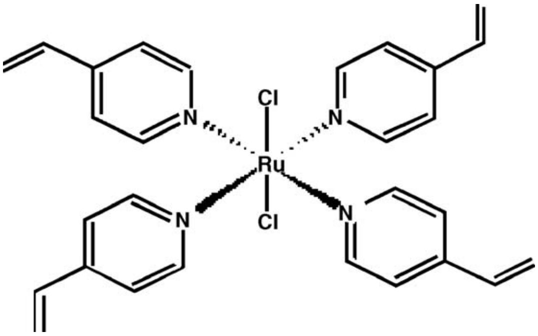

Fig. 1. Proposed structure for *trans*-[$RuCl_2(vpy)_4$].

way to incorporate redox groups into polymeric films by direct preparation of a binary copolymer from a styrene (ST) monomer and a monomer containing a transition metal complex to yield an in-chain transition metal coordination polymer. This paper focuses on the synthesis and characterization of an electroactive binary copolymer containing an in-chain metal center, through the chemical synthesis of styrene (ST) with benzoyl peroxide (BPO) in the presence of a comonomer *trans*-[$RuCl_2(vpy)_4$]) complex bearing a four ligand 4-vinylpyridine (vpy) coordinated to ruthenium metal ion, as shown in Fig. 1.

The resulting polymer maintains the desirable thermo mechanical properties of polystyrene and chromophicity of the ruthenium complex, bearing a new material to be utilized in a wide variety of applications. The stability of the polymer-metal complex is a fundamental requirement for several applications. In this respect, the use of *trans*-[$RuCl_2(vpy)_4$]) is highly promising, since these in-chain transition metals form highly stable complexes with interesting physical properties.

## 2. Experimental

### 2.1. Reagents and synthesis

Commercially available analytical grade reagents were employed throughout this study. $RuCl_3.3H_2O$ (Aldrich) and 4-vinylpyridine (vpy) (Aldrich) were used without further purification. The synthesis method used to produce the ruthenium blue solution and *trans*-[$RuCl_2(vpy)_4$] is described elsewhere [6,7].

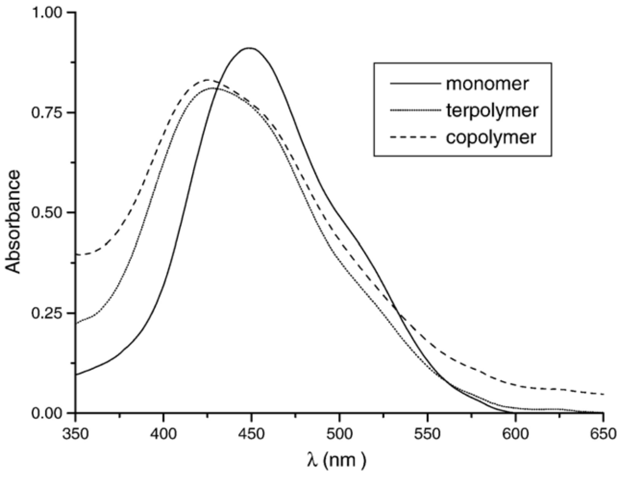

Fig. 2. Electronic spectra for the monomer, copolymer and terpolymer in $CH_2Cl_2$.

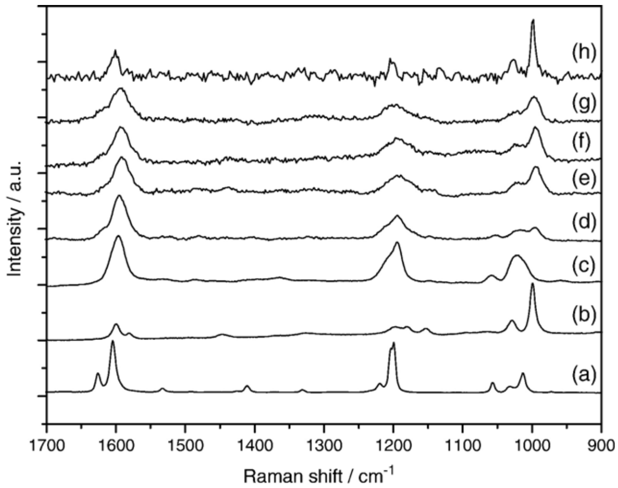

Fig. 3. Raman spectra of (a) *trans*-[$RuCl_2(vpy)_4$]; (b) polystyrene; (c) poly-{*trans* [$RuCl_2(vpy)_4$]}; (d) copolymer 1; (e) copolymer 2; (f) copolymer 3; (g) copolymer 4; (h) terpolymer. Spectra (a) to (c) excited by the 632.8 nm and (d) to (h) excited by the 514.5 nm lines.

### 2.2. Synthesis of poly-{trans-[RuCl2(vpy)4]-co-styrene}

0.05 g (0.2 mmol) of benzoyl peroxide (BPO) was dissolved in 1 mL (9.8 mmol) of toluene and to this solution 0.09 g (0.15 mmol) of *trans*-[$RuCl_2(vpy)_4$] (vpy=4-vinylpyridine) dissolved in 15.00 mL of styrene (ST) was added. The temperature was kept around 100+2 °C and the reaction was completed after 6 h (sample 1). For sample 2, the conditions were the same as those used for sample 1, except that the amount of *trans*-[$RuCl_2(vpy)_4$] was 0.045 g (0.076 mmol). For samples 3 and 4, conditions were the same as those used for sample 2, except that the reaction time was 12 h. The syntheses were conducted under inert Ar atmosphere.

### 2.3. Synthesis of poly-{trans-[$RuCl_2(vpy)_4$]-4 vinylpyridine-styrene

The synthesis of this terpolymer was performed in a similar way to that of the copolymer, except that the amount of ST (7.5 ml) and 4-vinylpyridine (7.5 ml) were different. The total reaction time was 3 h at 120+2 °C. The syntheses were conducted under inert Ar atmosphere.

### 2.4. UV–vis spectroscopy

The electronic spectra for *trans*-[$RuCl_2(vpy)_4$] (I), poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene} (II) and I poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene-4-vinylpyridine} (III) were obtained in $CH_2Cl_2$ with an ZEISS spectrophotometer, model Specord M500. All the measurements were carried out in quartz cuvettes with an optical path of 1.00 cm.

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