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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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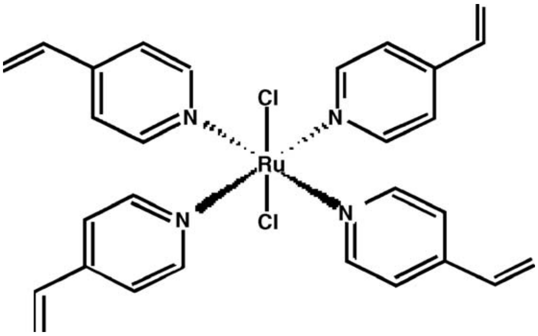

Fig. 1. Proposed structure for *trans*-[RuCl$_2$(vpy)$_4$].

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$_2$O (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].

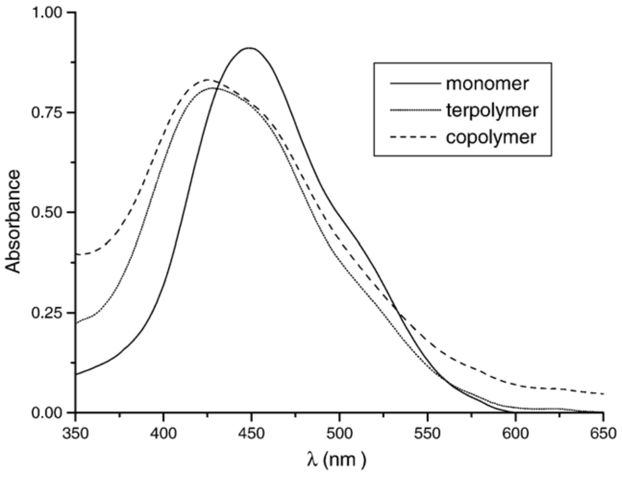

Fig. 2. Electronic spectra for the monomer, copolymer and terpolymer in CH$_2$Cl$_2$.

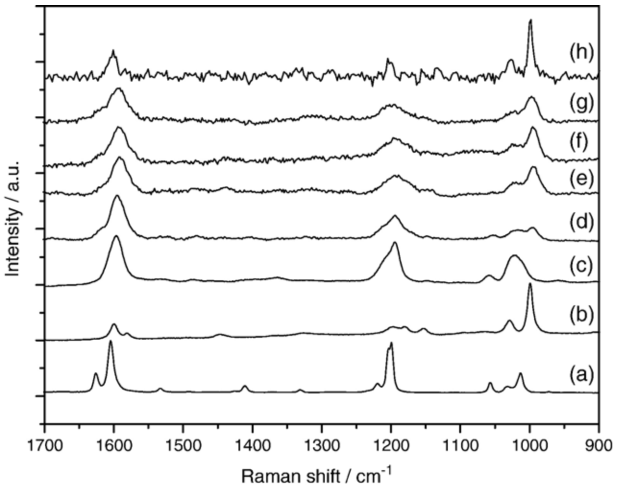

Fig. 3. Raman spectra of (a) *trans*-[RuCl$_2$(vpy)$_4$]; (b) polystyrene; (c) poly-{*trans* [RuCl$_2$(vpy)$_4$]}; (d) copolymer 1; (e) copolymer 2; (f) copolymer 3; (g) copolymer 4; (h) terpolymer. Spectra (a) to (c) excited by the 632.8 nm and (d) to (h) excited by the 514.5 nm lines.

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$_2$Cl$_2$ with an ZEISS spectrophotometer, model Specord M500. All the measurements were carried out in quartz cuvettes with an optical path of 1.00 cm.

Table 1
Vibrational frequencies (cm^{-1}) of *trans*-$[RuCl_2(vpy)_4]$, polystyrene, poly-*trans* $[RuCl_2(vpy)_4]$ (obtained by electrochemical synthesis), copolymers 1 to 4, and the terpolymer

trans-$[RuCl_2(vpy)_4]$	Polystyrene	Poly-{*trans*-$[RuCl_2(vpy)_4]$}	Copolymer 1	Copolymer 2 to 4	Terpolymer
1013	999		996	995	999
1033	1030	1022	1021	1023	1027
1057		1059	1053		
	1153				
	1180				
1200	1198	1194	1194	1193	1201
1204		1207 (sh)	1209 (sh)		
1220					
	1581				
1604	1600	1597	1595	1594	1601
1625					

sh = shoulder.

2.5. Raman spectroscopy

Raman spectra were obtained with a Renishaw Raman System 3000 equipped with a CCD, using either the 632.8 nm line of an He-Ne laser (Spectra-Physics model 127) or the 514.5 nm line of an Argon ion laser (Omnichrome), for the copolymers 1 to 4. The laser was focused onto the sample surface by means of a microscope (Olympus BH2T) and the laser power was kept at 3 mW. The powdered samples were pressed onto a microscope slide. The spectral resolution employed was 4 cm^{-1}.

2.6. Thermal analysis

Thermal stability and thermal transitions of the copolymer and terpolymer were observed by thermogravimetric analysis using a Shimadzu TGA-50 from 25 to 600 °C (10 °C min^{-1}) and a Shimadzu DSC-50 from 25 to 200 °C (10 °C min^{-1}), under N_2 atmosphere (50 mL min^{-1}).

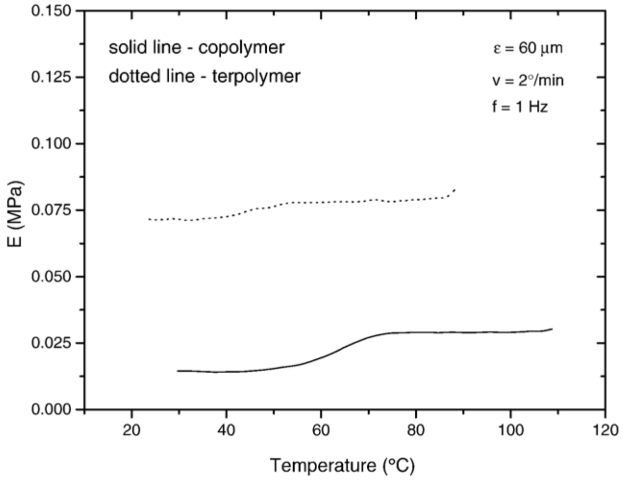

Fig. 4. (a)Dependence of sample storage modulus (E) for the copolymer and the terpolymer. Sample thickness was 0.35 mm.

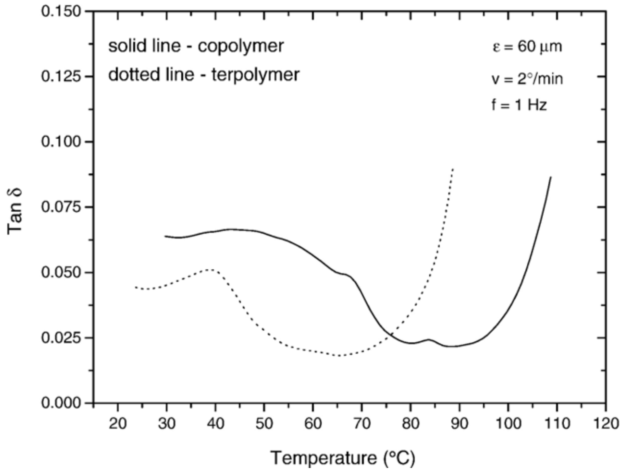

Fig. 5. Tan δ vs temperature for the copolymer and the terpolymer. Sample thickness was 0.35 mm.

2.7. DTMA

Dynamic–thermal–mechanical analysis was carried out using a mechanical spectrometer DTMA *NETZSCH*, model 242, analyzed under compression load with a frequency of 1 Hz and a heating rate of 2 °C min^{-1}.

2.8. SEM

Microscopic analysis was carried out using a scanning electron microscope (Philips X30) with an EDS (EDAX) probe.

3. Results and discussion

3.1. UV–vis spectroscopy

The monomer complex shows a band with λ_{max} at 448 nm and a shoulder at ca. 520 nm. These bands have previously been described by Franco and colleagues [8–10]. For the copolymer and terpolymer the monomer band at 448 nm is shifted to ca. 428 nm. Shoulders at ca. 450 and 510 nm were also observed in the copolymer spectrum, these two bands probably being the residual complex monomer bands. The hypsochromic shift of the 448 nm monomer complex band to 428 nm can be initially attributed to two factors: the first being the change in the complex coordination sphere after polymerization, resulting from the rigid polymeric backbone, which would imply a greater reorganization energy; the second one being the chemical coordination of the vinyl group (unsaturated) after the polymerization, which suppresses the conjugation with the pyridine ring. A similar complex, with no vinyl substituent in the pyridine ring, *trans*-$[RuCl_2(py)_4]$, in chloroform, has a band with λ_{max} at 398 nm, which confirms the second hypothesis, as in this case there is no effect due to the ring substituent. [11]. Additionally, neither the formation of new bands nor the suppression of the existing bands was observed, which means that the complex integrity was maintained after the polymerization. Fig. 2 shows the spectra of the monomer, copolymer and terpolymer.

3.2. Raman spectroscopy

The Raman spectrum of the solid monomer complex [12] has previously been reported as having several bands assigned to the pyridine ring and vinyl group modes. Fig. 3 shows the Raman spectra for the copolymer samples 1, 2, 3, 4 and the terpolymer along with the spectra of complex monomer *trans*-[$RuCl_2(vpy)_4$], polystyrene and poly-{*trans*-[$RuCl_2(vpy)_4$]} obtained by electrochemical polymerization [12].

The typical vibrational frequencies of *trans*-[$RuCl_2(vpy)_4$], polystyrene and poly-{*trans* [$RuCl_2(vpy)_4$]}, copolymers (samples 1 to 4) and the terpolymer are presented in Table 1.

The band at 996 cm^{-1} in copolymer 1 is assigned to polystyrene. The bands at 1021, 1053 and 1194 cm^{-1} are assigned to poly-{*trans*-[$RuCl_2(vpy)_4$]}. Polystyrene also shows a band close to 1194 cm^{-1}, associated with another two bands (1153 and 1180 cm^{-1}), and since in the case of the copolymer 1 spectrum these two bands are absent, this band at 1194 cm^{-1} must be due to poly-{*trans* [$RuCl_2(vpy)_4$]}. The band at 1595 cm^{-1} is assigned to poly-{*trans*-[$RuCl_2(vpy)_4$]} and polystyrene, because both have bands near to this wavenumber. In all samples analyzed one can verify the absence of a band at 1625 cm^{-1} (stretching of the C═C vinyl group of the complex) and at 1629 cm^{-1} (stretching of the C═C vinyl group of styrene) [13], which clearly indicates the completion of the polymerization process. The copolymers 2, 3 and 4, prepared with a lower concentration of the monomer metal complexes, show a visible increase in the intensity of the band at 996 cm^{-1}, due to the polystyrene, in relation to the bands assigned to the polymerized metal complex, as compared to copolymer 1 with the highest concentration of *trans*-[$RuCl_2(vpy)_4$]. This change in the relative intensity of the bands due to the polymerized metal complex and polystyrene reflects the sensitivity of Raman spectroscopy to the concentration, especially in the presence of a chromophore, when resonance Raman enhancement is operative. The terpolymer spectrum has much weaker signal intensity, probably due to the film being thinner in comparison to the copolymer samples. The terpolymer spectrum resembles that of the polystyrene, noticeably in the bands around 1000 and 1600 cm^{-1}, however, the band at 1200 cm^{-1} can be assigned to poly-{*trans*-[$RuCl_2(vpy)_4$]}. These features indicate a lower concentration of complex in the terpolymer compared to copolymer. The bands due to vinyl *ν*(C═C) are absent, indicating the almost complete polymerization of the monomer complex, styrene and vinylpyridine.

3.3. Thermal analysis

3.3.1. TGA

Thermal Gravimetric Analysis (TGA) was performed on the poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene} and terpolymer poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene-4-vinylpyridine}. For the terpolymer a significant loss of mass (13%) was found in the interval from 35 to 300 °C. After reaching a temperature of 390 °C mass loss takes place due to terpolymer decomposition, reaching a maximum at 427 °C, where approximately 85% mass loss is observed. For the copolymer poly-{*trans*-[$RuCl_2(vpy)_4$]-co-styrene} the mass loss was around 8% in the interval from 60 to 325 °C with a similar behavior being observed for the terpolymer. The onset of the decomposition was at about 412 °C, with a mass loss of 86% being observed when the temperature reached 440 °C. This loss was less pronounced in the copolymer. In both cases the mass loss is due to solvent molecules, monomers, oligomers and initiators.

3.3.2. DSC

The DSC curve for the copolymer recorded in the interval from 20 to 200 °C reveals a T_g (vitreous transition) at 69.98 °C. This value is lower than the corresponding value for polystyrene (around 100 °C). An additional exothermic peak is observed at 182 °C, this value being attributed to the polymerization reactions of the residual unreacted vinyl groups. The DSC curve for the terpolymer, registered in the interval 20 to 200 °C, reveals a T_g at 65.45 °C. This value is about 35 °C lower than the corresponding value for polystyrene. However, as these values are dependent on molecular weight, this displacement can be attributed to the low molecular weight of the terpolymer.

3.3.3. DTMA

Dynamic–thermal–mechanical analysis provides information on the influence of the different components on storage modulus (E) and the relation between energy dissipation and storage dynamic modules, tan δ, in the different samples, when submitted to mechanical–dynamic deformation in a temperature range. The measurement conditions are indicated on the graphs, that is, measurement amplitude 60 micrometers, heating rate 2 °C min^{-1} and input frequency 1 Hz.

Results from the DTMA are shown in Figs. 4 and 5, showing respectively the dependence of storage modulus (E) and the dissipation energy (δ) with the temperature, for both copolymer and the terpolymer. From the graphs, it is possible to conclude that:

i) The storage modulus E of the sample is greater for longer curing times. There is an increase in the storage modulus during the measurement which occurs at around 45 °C for the terpolymer and at 65 °C for the copolymer.
ii) The dissipation energy is greater for the copolymer at low temperatures, which indicates a greater mobility of some entity and thus the modulus is lower. As the mobility decreases or this entity rearranges, the storage modulus increases and the dissipation energy decreases.
iii) The increase in tan δ at higher temperatures, for both curves, is surprising since it does not correspond to the variation in the modulus.

4. Conclusions

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 was fully characterized by UV–vis. spectroscopy, thermal analysis, Raman spectroscopy and scanning electron microscopy (SEM). 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.

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