From Ruthenium Complexes to Novel Functional Nanocomposites: Development and Perspectives

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1. Introduction

Nanotechnology is one of the most widespread topics for current development in fundamentally all research areas. Along with polymer science that is also one of the leading fields and their studies cover a broad range of topics. This would include nanoelectronics as the critical scale for modern devices is now below 100 nm. Other research areas may include polymer-based biomaterials, such as miniemulsion particles for drug delivery or tissue engineering, self-assembled layer-by-layer polymer films, electrospun nanofibers and imprint lithography.

Although the terminology "Nanotechnology" is quite recent, prior polymer science studies involving nanoscale dimensions were used. For example, phase separated polymer blends regularly acquire nanoscale phase dimensions; asymmetric membranes often have nanoscale void structure; miniemulsion particles can be synthesized below 100 nm and interfacial phenomena in blends and composites involve nanoscale dimensions. At times, amphiphilic macromolecules are used to modify the nanoparticles surface. The most common functionality of these types of polymers is a lipophilic part intercalated with the existing aliphatic chains at the nanoparticles surface, covering, or maybe even completely encapsulating the original passivated nanoparticle.[1, 2] This type of encapsulation has been described for copolymers [3, 4] and phospholipids,[5-7], *inter alia* and takes advantage of the hydrophobic colloidal stability of organically passivated nanoparticles (NPs) to prepare polymeric nanocomposites. In this chapter we plan on reviewing various nanocomposites using a polymer-based matrix with transition metal complexes, namely ruthenium based complexes, and a wide range of inorganic nanoparticles with varying optical, antimicrobial and magnetic properties. These nanocomposites have potential applications in biomedical implants as well as small devices for clinical applications.

2. Metallopolymers

Recent interest in functional polymer matrix based nanocomposites has emerged with great importance in many fields of scientific research as well as in industrial applications, which will increase greatly due to the variety of possible modifications in the chemical and physical properties of these materials.[8] This well-known interest in soft functional materials, led to the growing realization that the presence of metal centers in macromolecular materials can result in enhanced novel properties while maintaining the capacity of polymerizing through classic processing methods. Metal centers have been neglected as important structural components of synthetic polymers although they play a key role in determining the functions of many extended solids and biological macromolecules. The metallopolymer field has been delayed due to synthesis and characterization problems, such as what procedures to use, purification issues and a lack of commercially available starting reagents. Most of the classic polymerization procedures used in pure organic monomers originated inefficient or undesirable side reactions with the presence of the metal centers. These classic procedures originated low molar mass metallopolymers, contaminated by structural defects or missing conclusive characterization. The end of last century dictated the beginning of high molar mass metallopolymers with defined microstructures. Most of the synthetic strategies used are either compatible with the presence of coordinated metal centers or with pendant ligands that tolerate the consequent incorporation of metal ions.[9-11] This progress has been supported by the discovery and expansion of new characterization techniques, such as matrix-assisted laser desorption/ionization–time of flight spectroscopy or electrospray ionization mass spectrometry, as well as the rekindling of more traditional methods, such as analytical ultracentrifugation, leading to a vast collection of metal containing polymers that display an array of bonding modes and an assortment of structures. The ability to prepare metallopolymers with a variety of structures has fuelled efforts to improve the efficiency and control of synthetic procedures in order to create scaled-up, well-defined materials. These accomplishments lead to a range of potential applications which have now emerged, and the aim of this chapter is to illustrate selected recent advances of the use of metallopolymers in sync with inorganic nanoparticles to produce nanocomposites with varying antiseptic, optical and magnetic properties. These nanocomposites have potential applications in biomedical implants as well as small devices for clinical applications.

Network polymers based on styrene, prepared by well-developed suspension polymerization processes, retain many of their qualities for a microcomposite host matrix. The many advantages include facile preparation, controlled surface area and porous structure, good thermal resistance and reasonable chemical inertness.[12] Styrene-divinylbenzene copolymers have been the subject of several studies. Mahdavian *et al.* described an easy and efficient method for preparing polymer-supported chiral copolymers of styrene-divinylbenzene, which can be used in chromatographic columns packing.[13] Crosslinked copolymers prepared from styrene-divinylbenzene are of particular interest when used in the preparation of ion exchange resins by the introduction of various functional groups (polar or not) as alkyl, benzoyl, acetyl, hydroxymethyl and sulfonic

derivatives.[14] Their main applicability is in catalytic supports and solid-phase extraction. The efficiency of sulfonate agents and their effects on the morphology of styrene-divinylbenzene beads have been investigated.[15] The authors found that the use of acetyl sulfate as a sulfonate agent preserved the spherical morphology of the beads.

Polymers based on the application of coordination forces have been prepared recently. The first direct synthesis of a polymer containing a transition metal complex gave rise to a coordination polymer based on ruthenium(II)-terpyridine complexes.[16,17] The combination of conventional polymers to metal centers generates intrinsic properties of the metal, retaining the properties of the conventional polymer. A new property acquired due to the metal center, is the electroactivity amongst all the transition metals, and the ruthenium has been widely used by coordination chemists mainly due to its ease of forming extremely stable complexes, especially with pyridine ligands and their derivatives.[18]

3. Ruthenium (II) complexes: a brief history

Ruthenium based metal complexes have shown a plethora of uses and applications. Namely, complex structures in the presence of a metal center containing ruthenium have shown good results in biological applications.[19-21] Coordination compounds of formula *trans*-[RuX$_2$(L)$_4$], where (X) = Cl, Br, and I, (L) one monodentated ligand (Figure 1) are extremely well known in literature and many compounds containing pyridine groups and their derivatives have been prepared and characterized.[22-24]
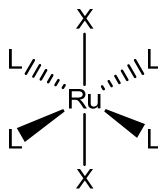

Figure 1. Molecular structure for ruthenium (II) metal complexes, where L is the different ligands monodentate and X, the halogens Cl, Br, I.[25]

The first studies were those with the synthesis of coordination complexes with four pyrrole group substituents. In 1996, progress was made in the synthesis and characterization of copper (I) complexes containing four tetranuclear pyrrole substituents attached to the pyridine ligand. The aim of the complex synthesis was to electropolymerize in the form of a copolymer, but the results were not encouraging and the authors remained focused only on the synthesis of the ruthenium complexes.[26] The preparation of a series of new electropolymerizable complexes with the general formula *trans*-[RuX$_2$(L)$_4$] was achieved.[27, 28] The preparation and full characterization of poly-*trans*-[RuCl$_2$(pmp)$_4$] (pmp=3-(pyrrol-1-ylmethyl) pyridine) was reported and its applicability demonstrated in the preparation of modified electrodes.[27, 29]

In order to fully understand the electropolymerization process and to determine the optimized electrochemical parameters for the achievement of a good film, electrochemical

studies were made on *trans*-[RuCl₂(pmp)₄]. In 1997, the preparation of electrodes modified by electropolymerization of poly-*trans*[RuCl₂(pmp)₄] using galvanostatic and potenciometric techniques was accomplished.[28] Studies show that water-soluble ruthenium complexes are of high therapeutic value due to their capacity to interfere with nitric oxide (NO) in biological systems.[30] On the other hand, the complex *trans*-[RuCl₂(vpy)₄] (vpy=4-vinylpyridine),[31] composed of four groups, which are easily polymerized producing electroactive adherent films, compared to films made from the linkers vinylpyridine and vinylterpyridine, were also prepared.[32, 33] Previous studies have shown that the complex *trans*-[RuCl₂(vpy)₄] can be electropolymerized on different substrates, including inert materials such as Pt and Pd,[31] ferrous alloys[34, 35] and stainless steel.[36] Studies of cyclic voltammetry, electrochemical crystal microbalance quartz and Raman spectroscopy revealed the results of electropolymerization of the complex *trans*-[RuCl₂(vpy)₄] in Au and Pt electrodes in particular the effects of the polymerization potential on the characteristics of the film formed, and especially the understanding of the key processes involved in electropolymerization.[37]

Much of the recent work on polymer substrates has been focused on the structure of the polymeric matrix for subsequent complex formation with a metal ion. Antony *et al.* studied the synthesis and catalytic properties of poly-(styrene-divinylbenzene) supported by ruthenium (III complexes.[38] Styrene-divinylbenzene copolymers, with its reactive groups, have often been used as ligands with chelating properties. When reacted together with styrene (sty), divinylbenzene (DVB) can be used as a reactive monomer in polyester resins. The resulting cross-linked polymer is mainly used for the production of ion exchange resin. The authors showed that by a simple method, the new polymer of ruthenium catalyst was effective in the epoxidation of styrene and cyclic olefins. The facile preparation and recyclability of these catalysts should provide a useful strategy for oxidation of organic substrates under controlled experimental conditions.
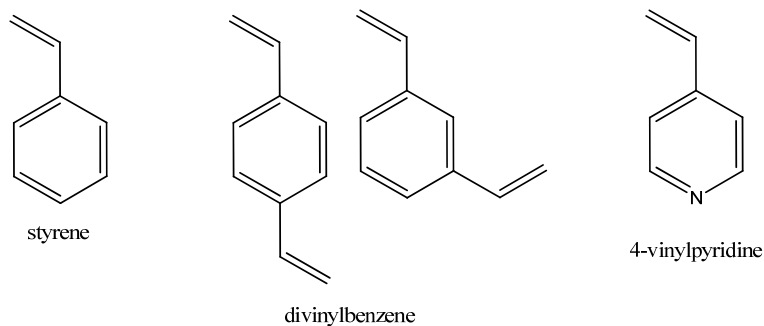

Figure 2. Chemical structures of monomers commonly used along with ruthenium complexes to form metallo-co-poymers.

However, few thermal studies were found in the literature involving copolymers of vinylpyridine and divinylbenzene. The vinylpyridine can be chemically modified by oxidation, producing vinylpyridine N-oxide. These modified materials can be used as

catalyst supports and ion exchange resins to remove heavy metals due to the presence of oxidized vinylpyridine groups.[39] The covalent incorporation of the transition metal complexes in the polymer network should be accompanied by benefits in biological systems.[40] There is great interest in biomedicine and bio-nanotechnology in studies involving supported metal complexes as enzyme inhibitors.[41] Metals such as ruthenium, osmium, and iridium are capable of forming stable complexes which are not involved in biological environments, thereby expanding the coordination modes limited to carbon. This provides new opportunities for the construction of small molecular structures that cannot be occupied by purely organic compounds.[42] Recent studies have shown the importance of the presence of ruthenium structures in biological research involving cancer treatment.[43] Lately, many studies are being conducted using ruthenium complexes in nanocomposites and biomaterials. Such studies have shown that the nanocomposite containing the complex can be used as nanodrug, for targeting cancer, and intracellular labeling.[44] Among the various research groups involved in this issue, Zhang *et al.* showed that the effect of nano-scale carborane ruthenium (II)-arene complexes, showed significant results in treating lung cancer.[45] The authors suggest that this complex containing Ru(II) may be a strong candidate for lung cancer chemotherapy. The results provide evidence that tumor growth can be inhibited by anti-cancer ruthenium (II) arene complex *in vivo*. Clearly, a better understanding of the mechanism of action and possible chemotherapeutic activity of the complex of Ru(II)-arene could certainly benefit the future clinical treatment of this cancer.

Although one may propose alternatives of the possible reaction mechanisms between the monomers: the *trans*-[RuCl$_2$(vpy)$_4$] complex, styrene, divinylbenzene and 4-vinylpyridine, it is not possible to safely affirm what structures will be formed by a combination of these monomers (Figure 2). However, the authors suggest that the formation of crosslinking between the complex combination with the monomers participating in the structure (Figure 3) is highly probable, where the polymerization and the polymeric chain propagation could occur in both, by double bond cleavage of the ligands of the metal complex (vpy) and the interpolation of the monomers (sty, DVB, vpy) among themselves. Thus, there is still no concrete answer on the exact formulation of co- and terpolymers synthesized. Efforts in this direction have been intensified by several researchers in order to have an idea of the structural composition of these polymers and how, or even if, these bonds significantly influence the formation of these new functional polymers nanocomposites.

In this chapter we plan on reviewing various nanocomposites using a polymer-based matrix with transition metal complexes and a wide range of inorganic nanoparticles with varying optical, antiseptic and magnetic properties, namely ZnO nanoparticles which have interesting optical properties; silver nanoparticles (AgNPs) which have antimicrobial properties as well as known optical properties and magnetic nanoparticles (CoPt$_3$) which have well-defined magnetic properties.

4. Inorganic nanoparticle incorporation

The incorporation of nanoparticles as a filler in polymer matrices is interesting mainly due to the different properties resulting therefrom and compared to their bulk analogues.
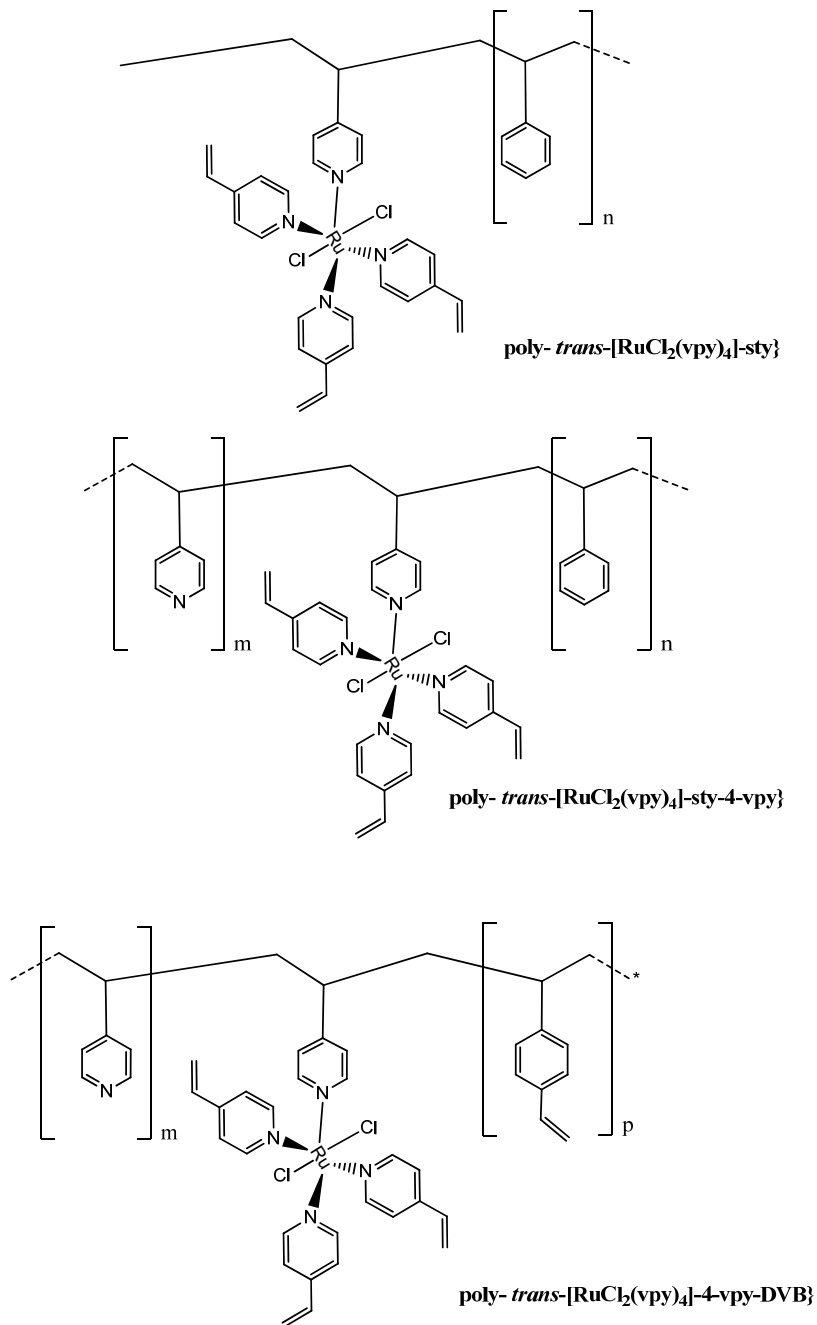
poly- *trans***-[RuCl₂(vpy)₄]-sty}**

poly- *trans***-[RuCl₂(vpy)₄]-sty-4-vpy}**

poly- *trans***-[RuCl₂(vpy)₄]-4-vpy-DVB}**

Figure 3. Proposed polymeric structure containing monomers: styrene, divinylbenzene, 4-vinylbenzene and ruthenium complex.

Several authors have described changes in optical, electrical and mechanical properties when the size of a certain material reduces to nanoscale dimensions.[46, 47] This type of interaction can influence the molecular dynamics of a polymer hence resulting in significant changes in their physical, thermal behavior and mechanical properties. Bullions *et al.* investigated a hybrid material consisting of NPs embedded in SiO_2 poly(imide).[48] The authors concluded that the formation of chemical bonds between the NPs and certain terminal groups of poly(imide), confines the space accessible to the polymer chains in the molecular dynamics influencing polymer, which can result in changes in thermal stability and consequently its glass transition temperature. A controlled polymer synthesis in the presence of inorganic NPs, allows rigorous control over the matrix's physical/chemical properties. Nonetheless, the chemical affinity between nanoparticles and polymer is a major aspect in nanocomposite preparation. The compatibility of the inorganic material with the polymer matrix can be improved through the chemical surface modification of the particles. At times, surface modification may be necessary to promote chemical compatibility between components. For example, in the case of trioctylphosphine oxide (TOPO)-prepared semiconductor nanoparticles, these can be used directly in the synthesis of an organic matrix-based nanocomposite, once these are passivated with molecules of hydrophilic nature.

For the preparation of nanocomposites there is a diversity of polymer synthesis techniques, the most common being: dispersion polymerization, mass polymerization and emulsion polymerization. Recently the development of new radical polymerization methods, currently denominated by controlled/"living" polymerization, came to ease new methodologies that are prepared in a controlled manner.[18] This method was used for various inorganic materials, such as TiO_2[49-51] and SiO_2,[52] where these were directly dispersed in the monomer. More recently the NP encapsulation by an *in situ* miniemulsion polymerization was demonstrated with poly-styrene,[53-55] poly-butyl acrylate[53, 56] and a poly-styrene - poly-methylmetacrylate copolymer.[57] However changes in the crystallization of semicrystalline polymer matrices in nanocomposites has also been described.[58] For example, a significant influence of NPs morphology on the crystallization kinetics of polyamide in a hybrid material consisting of an array of poly(tetramethylene terephthalamide) fibers or containing SiO_2 spheres with nanometric dimensions.[59] When preparing Bi_2S_3/Nylon nanocomposites, the authors found that the Bi_2S_3 nanofibers act as nucleation sites, resulting in a larger number of spherulites in the nanocomposite when compared to the pure polymer.

Depending on the envisioned application, various types of fillers may be used for loading the nanocomposite which may differ, for example, their morphological or other properties, such as heat resistance or chemical reactivity. Studies have shown that for the incorporation of metal and semiconductor NPs in this polymeric matrix, these nanoparticles can be dispersed among the crosslinking of the polymeric matrix, as shown in the Figure 4. Amongst the most common fillers for polymer-based nanocomposites are carbonates, sulfates, alumino-silicates and metal oxides (Al_2O_3, Fe_2O_3, ZnO).[60] Semiconductor NPs such as CdS, ZnS, or CdSe have also been widely used due to their optical properties.[61, 62] Some of the examples of inorganic particles cited in the literature are the use of TiO_2 NPs in
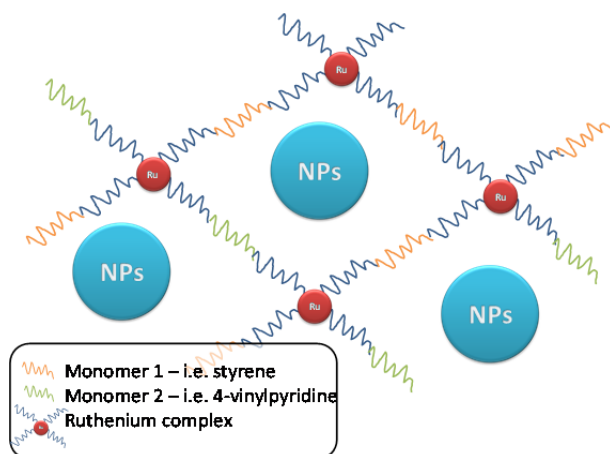
Figure 4. Proposed crosslinked structure of prepared metallpolymers nanocomposite.

the preparation of composites for paints and coatings[46, 63] and SiO$_2$ NPs, which can give added strength or flame retardant characteristics to nanocomposites.[64, 65]

5. Ruthenium complex based copolymers with incorporated inorganic nanoparticles

The following section summarizes relevant properties of functional ruthenium based nanocomposites when doped with diverse inorganic nanoparticles (magnetic, antimicrobial and luminescent nanoparticles).

5.1. ZnO NP doped Ru complex/styrene copolymer

Semiconductor NPs show size-dependent optical properties and have been widely explored as new optical materials.[47] New optically active inorganic/polymer nanocomposite have been prepared when using semiconductor NPs together with polymers. As with all nanocomposites the intrinsic properties of the starting materials maintain but new properties due to synergistic effects arising from the combination of the inorganic and organic components may arise.[66] The homogeneous distribution of inorganic NPs within the polymer matrix and the strong interface adhesion between the matrix and nano-fillers are important aspects to be considered because of their influence in the nanocomposites' performance.[67] Segala *et al*. reported the preparation of nanocomposites containing ZnO NPs dispersed in the co-polymer poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty}.[68] The polymer was prepared through reaction of the complex *trans*-[RuCl$_2$(vpy)$_4$] with styrene.[69]

The ZnO NPs were previously prepared and their optical properties monitored by UV-visible spectrocsopy and size through high resolution transmission electron microscopy (HR-TEM) (Figure 5). A quantum mechanical effect occurring in the semiconductor NPs is the increase in band gap, with the reduction in particle size. The quantum confinement

effect is clearly seen in Figure 5 inset. The literature shows that bulk ZnO exhibit a band gap of 3.37 eV (or about 368 nm), whereas the NPs band gap has a characteristic optical feature at 357 nm. Theoretical calculations based on the effective mass approximation for spherical particles[70, 71] provides a size estimate of 5.2 nm diameter of the ZnO NPs. The size of the NPs was confirmed through HR-TEM in which the approximate size is in the order of 5 nm.
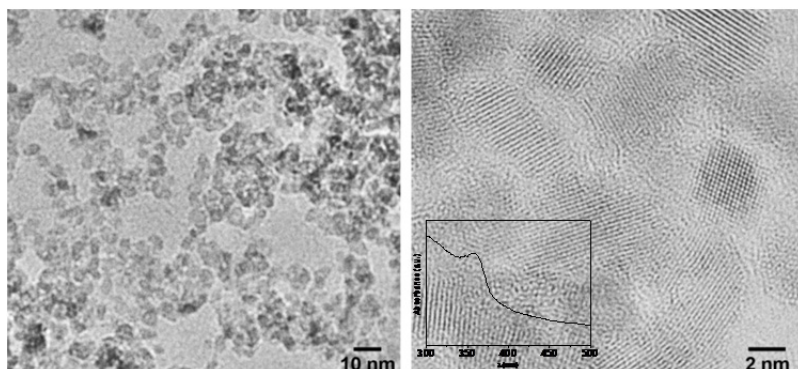

Figure 5. HR-TEM images of ZnO NPs used in the preparation of the nanocomposite. Inset: Optical spectrum of coloidal suspension of ZnO NPs.

When incorporating the semiconductor NPs into the copolymer matrix, the properties of the initial NPs were maintained, such as optical and structural properties.[68] Scanning electron microscopy (SEM) of the nanocomposite and energy-dispersive X-ray spectroscopy (EDS), clearly demonstrate the homogeneous presence of Zn and Ru throughout the whole sample. (Figure 6).

Nanocomposites containing ZnO and poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty} have been prepared and the results point to a homogeneous nanocomposite.[68] This study allows further development of this synthetic strategy to obtain homogeneous nanocomposites of variable composition that can find practical interest in ruthenium-based sensor devices.
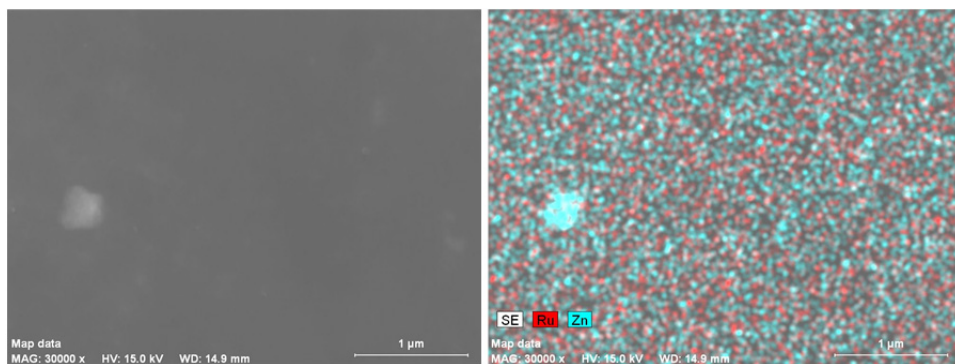

Figure 6. SEM image and EDS mapping of ZnO NPs dispersed in the co-polymer poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty}

5.2. Ag NP doped Ru complex/styrene/divinylbenzene copolymer

The bactericidal effects of ionic silver are well-known and have been used since ancient times. The precious metal was originally used as an effective antimicrobial agent and is relatively free of side effects. However, with the development of modern antibiotics to treat infectious disease, the use of silver in the clinical setting has been limited predominantly to topical cream based silver sulfadiazine to prevent infections associated with treatment of burns.[72-74] However recent studies revealed that Ag NPs have improved antibacterial properties when compared with bulk silver and that even nanomolar concentrations of Ag NPs can be more effective than micromolar concentrations of silver ions,[75] thus leading to an increased interest on materials containing nano-silver. Silver ions are known to be extremely reactive and could readily bind with an assortment of negatively charged molecules such as inorganic anions, proteins, RNA and DNA. Consequently, the antibacterial property of silver ions has been credited to its interaction with thiols, along with other groups such as carboxylates, phosphates, hydroxyls, imidazoles, indoles and amines. Roe and coworkers developed a method to coat plastic catheters with bioactive Ag NPs. The catheters are non-toxic devices capable of targeted and sustained release of bactericidal silver at the implantation site and were useful in preventing infectious complications in patients.[76] Bowler *et al.* assessed the antimicrobial properties of an absorbent topical wound dressing containing ionic silver, samples were tested with a diversity of known burn wound pathogens in a simulated wound fluid model. and verified that the silver-containing dressing is likely to provide a barrier to infection in controlling partial-thickness burns.[72] A relevant factor in the evaluation of biocide action of different materials is their behavior against the bactericidal dose-dependent effect on the different strains of bacteria. Because of the complexity in determining the actual bioavailability of Ag, values of minimum inhibitory concentration of about 100 strains of *Staphylococcus aureus* was reported, with a range 8-80 mg/L when using $AgNO_3$.[77] Similarly, minimum inhibitory concentration values for Ag studied with approximately 100 strains of *Pseudomonas aeruginosa* showed a range of 8 to 70 mg/L. These studies showed that some strains are resistant to Ag, and in fact, resistant strains of bacteria were isolated more than 70 years ago and its mechanism of resistance to Ag has been investigated.[77, 78]

Dutra *et al.* reported the preparation and characterization of the nanocomposite between a poly-{*trans*-[RuCl_2(vpy)_4]-styrene-divinylbenzene} or styrene-divinylbenzene-4-vinylpiridine matrix containing Ag NPs.[79] Non-aqueous polymerization using benzoyl peroxide as the initiator was the method used to prepare these materials. The Ag NPs were obtained through the chemical reduction using $NaBH_4$ as reducing agent and sodium citrate as stabilizer.[80] The Ag NPs optical properties were monitored by UV-visible spectroscopy and size and morphology confirmed through TEM. The nanocomposites morphology was characterized by Field Emission Gun Scanning Electron Microscope (FEG-SEM) and the thermal properties were studied.
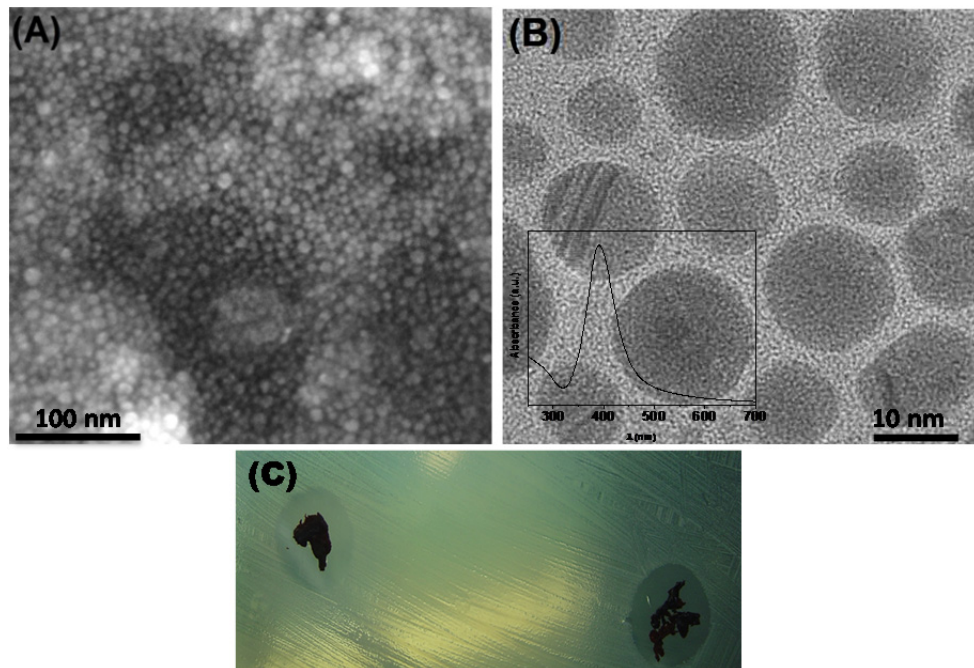
Figure 7. a) FEG-SEM image and b) HR-TEM image of silver nanoparticles. Inset: optical spectrum of AgNPs and c) Photograph of microculture plate containing the microorganism *Staphylococcus aureus* in the presence of poly-{*trans*-[RuCl$_2$(vpy)$_4$]-styrene–divinylbenzene}/AgNPs nanocomposite.

The antimicrobial action of the nanocomposite was evaluated using various microorganisms: *Staphylococcus aureus* and *Escherichia coli* and was confirmed by the presence of an inhibition halo of the bacterial growth in seeded culture media (Figure 7c). This growth inhibition caused by the presence of silver nanoparticles in the polymer reveals the antiseptic properties of the material. Authors suggested that the absence of ruthenium complex in the polymeric matrix interfered with the release of silver ions into the media, not conferring this material antimicrobial activity. The antimicrobial activity of the silver in the polymeric matrix can also be important for the prevention of proliferation of adherent bacteria in the surface of the polymeric materials, increasing like this the materials' lifetime. Polymeric matrix impregnated with Ag NPs ensures new surface properties that perform in the prevention of microorganism's adherence on the surface and deposits of proteins.

5.3. Magnetic NP doped Ru complex/styrene/divinylbenzene copolymer

Magnetic NPs are of great interest to researchers and cover a wide subject area, including magnetic fluids, catalysts, biotechnology, magnetic resonance imaging, prevention of the environment, among others.[81] Although a reasonable amount of methods have been developed for the synthesis of magnetic NPs with a wide variety of different compositions, the successful application of these magnetic NPs depend on their stability under different

conditions. In most applications, the particles properties are enhanced when present in the 10-20 nm size range. However, depending on the application, an inevitable problem associated with the particle size is its intrinsic instability over time has to be regarded. Some smaller particles tend to form agglomerates to reduce the energy associated with large surface area relative to the volume of nanometric particles. For most applications it is crucial to develop strategies to protect the chemical stability of the NPs in relation to the magnetic degradation during and after the synthesis. These strategies include coating with organic species, including surfactants or polymers, or a coating with an inorganic layer such as silica or carbon. It is notable that in many cases, protection of the particles or coating not only stabilizes NPs, but may also be used for additional functionality, for example, with NP or other ligands, depending on the desired application.[81] Several syntheses of Fe, Co, FePt and $Fe_xCo_yPt_{100-x-y}$ NPs have recently been developed to produce particles of controlled size and narrow size distributions. They are currently the focus of scientific research aimed at understanding the formation mechanism of monodisperse NPs and the influence of size and shape in their magnetic behaviour.[82] The literature reports the preparation of polydisperse 2 nm-sized alloy of Co-Pt prepared from organometallic precursors in the presence of a polymer.[83-85]

On the other hand, researchers at Ohio State University reported the development of magnetic NPs that promises rapid detection and elimination of the bacteria *Escherichia coli* (*E.coli*), anthrax *(Bacillus anthracis)* and other bacteria harmful to human health.[86] These studies have demonstrated the potential of the magnetic NPs studied and their aid in the rapid detection of *E.coli* strains in approximately five minutes, and removing 88% of the bacteria by providing a very attractive field for the decontamination of pathogenic microbes and diagnostic applications.[86] These studies were pioneers in using magnetic NPs to detect, quantify and differentiate *E.coli* cells.

A promising application of magnetic NPs is as drug carriers as well as in drug release, initially proposed by Widder *et al*. in the 70's.[87] The magnetic drug carriers have the potential to carry a large amount of drug to a certain body part, thus avoiding toxicity and adverse effects of excessive use of a large dose of drugs in the body. Although to date, there has been a breakthrough in *in vivo* applications, clinical studies in real situations are still problematic. Many fundamental issues in systems for controlled drug release need to be resolved, such as size-controlled synthesis and stability of the magnetic NPs, the biocompatibility of the coating layers (polymer or silica), links between drug-particle, among other physiological parameters.[81]

The literature describes various synthesis methods of interest to develop new bio-magnetic nanocomposite applications.[56, 88] However, some of these proposed methods suggest a post-synthetic step in order to prevent the liberation of the magnetic NPs. To investigate this authors have proposed an *in situ* synthetic method to incorporate the magnetic NPs during the synthesis of the nanocomposite. This section will present some results obtained in the preparation and characterization of magnetic $CoPt_3$ NPs and *in situ* incorporation of these particles in the poly-*{trans*-[$RuCl_2$(vpy)$_4$]-sty} polymer matrix. Although these

nanocomposites are not to be directly applied in Nanomedicine they may provide useful clues in the formulation of other materials.

The magnetic $CoPt_3$ NPs were characterized by UV-vis spectroscopy (Figure 8-inset).The optical spectrum of the magnetic NPs presents two characteristic bands, at 319 nm and 407 nm. The observation of the UV/vis spectra obtained from the starting materials, ie, salts of Co (II) and Pt (VI) in ethylene glycol showed an intense band at 522 nm for the Co (II) and two minor bands intensity for Pt (VI), 363 nm and 458 nm. However, the optical spectrum obtained for this alloy shows distinct bands of the starting materials, which indicates the presence of magnetic material, $CoPt_3$.[82] The morphology of the $CoPt_3$ NPs was analyzed by SEM and EDX confirmed the presence of metals in the magnetic alloy, and its respective mean ratio, Co:Pt, 1:3 (Figure 8). The presence of spherical agglomerates was observed by coalescence of smaller particles. However, the nanoscale of the $CoPt_3$ NPs was confirmed by TEM. Figure 8(right) shows TEM images obtained from a sample of these magnetic particles.
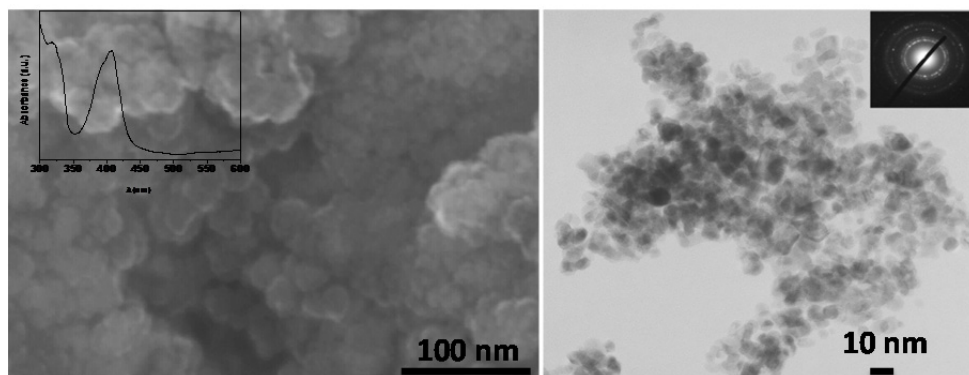

Figure 8. SEM image (left) with inset optical spectrum and TEM image (right) of $CoPt_3$ NPs.

The nanocomposite $CoPt_3$/poly-{*trans*-[RuCl_2(vpy)_4]-sty} was synthesized using the *in situ* method with a nominal percentage of 0.5%(w/w) $CoPt_3$ in relation with the styrene monomer and the complex *trans*-[RuCl_2(vpy)_4]-sty] and characterized by UV-vis spectroscopy. The optical spectrum of the magnetic nanocomposite present bands in the region of 320 to 410 nm (Figure 9b). A shoulder and band broadening observed in the 450 nm region of the optical spectrum, may suggest the overlap of the bands that characterize the complex *trans*-[RuCl_2(vpy)_4] with the magnetic NPs characteristic band. The morphology of the magnetic nanocomposite was analyzed simultaneously by SEM and TEM and the presence of the nanoparticles homogeneously dispersed in the polymeric matrix was observed. However, there are dots and small beads over the whole surface of the nanocomposite examined by SEM, suggesting an agglomeration of magnetic NPs incorporated in the copolymer matrix. The average size of the NPs is in the 10 nm range, showing that the average size of NP was not significantly altered during the synthesis of the nanocomposite. Larger particles are probably caused by coalescence of smaller particles.

EDX mapping was made on the SEM image of the nanocomposite and showed the homogenous presence of the CoPt$_3$ alloy over the entire surface of the polymer matrix.
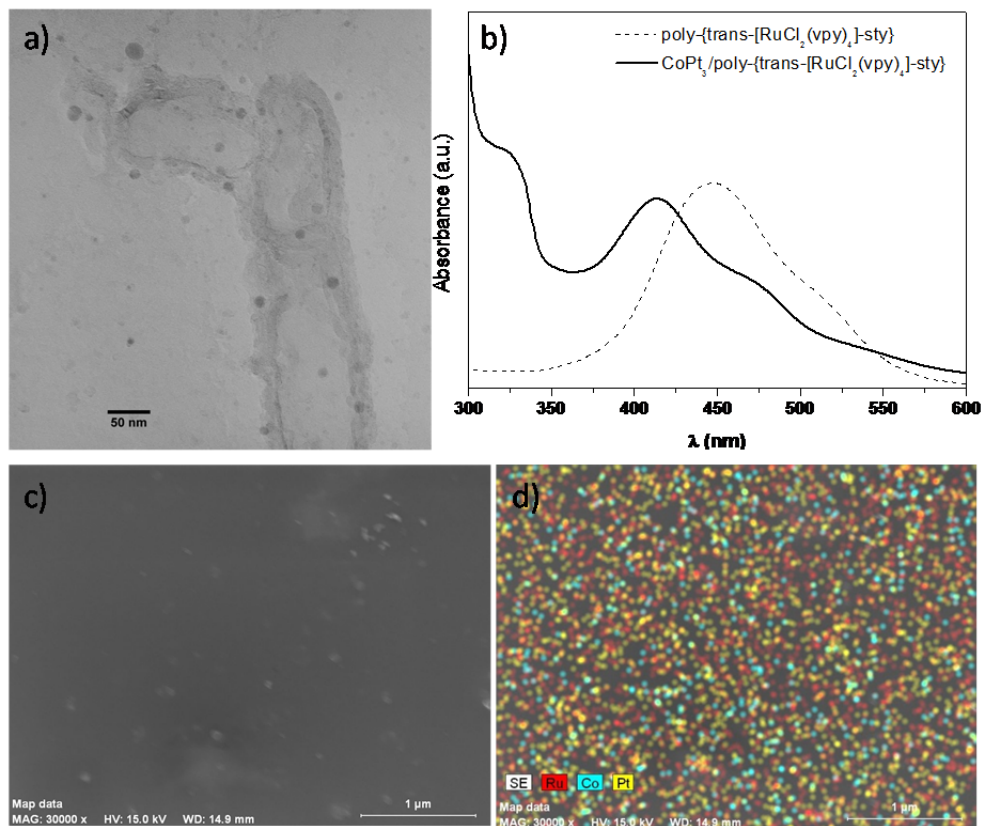

Figure 9. a) TEM image; b) optical spectra; c) SEM image and d) EDS mapping of the nanocomposite CoPt$_3$/poly-*{trans*- [RuCl$_2$(vpy)$_4$]-sty} 0.5%.

6. Concluding remarks and future trends

In this chapter we have discussed studies involving nanocomposites prepared from the complex *trans*-[RuCl$_2$(vpy)$_4$], with the monomers styrene, divinylbenzene and 4-vinylpyridine, with the incorporation of functional nanoparticles. To each type of nanoparticles, different properties may be attributed: (1) antimicrobial properties in the presence of Ag NPs, (2) luminescent properties in the presence of ZnO NPs and (3) magnetic properties of the alloy in the presence of CoPt$_3$. The Ag NPs precursors of antibacterial nanocomposites were prepared and characterized. The synthesis of the copolymers were carried out in these emulsions in the presence of complex *trans*-[RuCl$_2$(vpy)$_4$] monomer and other monomers such sty, DVB and vpy, which will form the polymeric matrices. These nanocomposites were characterized by optical, structural and

morphological techniques through UV-visible spectroscopy, SEM and TEM analysis. The antiseptic property of these new nanocomposite materials was confirmed by microbiological testing using the *Gram-positive*, *S. aureus* (ATCC-25923) and *Gram-negative*, *E. coli* (ATCC-25922) for Ag NPs impregnated with the polymer. The nanocomposites containing ZnO NPs with luminescent properties incorporated in the copolymers poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty showed that the synthesis method using *in situ* promotes better dispersion and a better distribution of the ZnO NPs along the polymeric matrix compared with the nanocomposite prepared by the analogous *ex situ* method. ZnO/poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty}nanocomposites prepared were fully characterized at the optical, structural and morphological level, through the techniques of UV-vis spectroscopy, analysis by SEM and TEM. CoPt$_3$ NPs, with superparamagnetic properties, were incorporated into a magnetic poly-{*trans*-[RuCl$_2$(vpy)$_4$]-sty} nanocomposite prepared and characterized. TEM images show that CoPt$_3$ NPs remained unchanged and are homogeneously embedded through the polymeric matrix of the magnetic nanocomposite The development of highly technological materials with antiseptic, optical and magnetic properties present in ruthenium complexes with biological activity are promising therapeutic applications with a high possibility of success if applied in the medical field and a variety of technological applications.

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Acknowledgement

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