



# Preparation and characterization of polystyrene-*b*-poly(2-vinylpyridine) coordinated to metal or metal ion nanoparticles

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## ABSTRACT

In this study, Co, Cr or Au<sup>3+</sup> functional polystyrene-*b*-poly(2-vinylpyridine), PS-*b*-P2VP complexes were prepared and characterized. Coordination of metal atom or ion to nitrogen atom of pyridine rings was confirmed by FTIR analyses. The strength and efficiency of coordination of P2VP blocks to Co, Cr or Au<sup>3+</sup> mainly depends on charge and stability of the complex formed that is mainly related to the energy of d orbitals. The results reveal that the thermal stability of the polymer composite formed increases with the increase in strength of the coordination. Changes in thermal decomposition mechanism and product distribution were recorded. Degradation of P2VP units coordinated to Cr, Co or Au<sup>3+</sup> was started by loss of pyridine units leaving an unsaturated and/or crosslinked polymer backbone that degraded at relatively high temperatures.

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## 1. Introduction

Nanostructures have received great attention recently due to their special optical, electronic, magnetic and chemical properties [1–5]. The most popular approach involves the synthesis of nanoparticles in situ within the block copolymer template by using preformed micelles of block copolymers containing metal precursors [6–11]. As a consequence of the strong affinity of the amines to various ions and polar groups, the polymers containing a pyridine moiety can make strong bonds with various metal ions or nanoparticles and have attracted increasing attention.

In recent studies, poly(vinylpyridine) (PVP) was widely used to synthesize nanoparticles by itself as well as in combination with other polymers. Block copolymers with the ability to form stable micelles in solution and at interfaces are excellent candidates for the preparation of various metal nanoparticles with a narrow size distribution and long-term stability [12–17].

For example, Moeller et al. [15,16] has prepared gold nanoparticles with the use of polystyrene-*b*-poly-2-vinylpyridine (PS-*b*-P2VP) copolymer for the first time. The metal salts formed complexes with the pendant pyridine rings, concentrating the metal ions in the poly-2-vinylpyridine domains. Lohmueller et al.

[17] fabricated various metal nanoparticles (Au, Pt, and Pd) packed in quasi-hexagonal ordering using PS-*b*-P2VP micelles. The size of nanoparticles was controlled by the immersion time into a solution containing metal precursors.

Coordination of metal/metal ion improves the thermal stability of the host polymer [18–22]. Zander et al. [22], studied the thermal characterization of poly(4-vinylpyridine) crosslinked with metal salts and suggested that Tg enhancement was highly dependent upon the type and loading of the metal salt. Wu et al. [21] investigated Tg value of poly(4-vinylpyridine) copolymer and its complex with transition metal ion and determined that Tg increases with increasing the metal ions content. The result reveals that upon coordination of the pyridine rings to the metal ions the intermolecular interactions are enhanced.

However, the knowledge of thermal characteristics and degradation mechanisms of these composites that are very important for investigation of application areas is still limited. Among the several thermal analysis methods, direct pyrolysis mass spectrometry (DP-MS) is the only one that gives information on not only thermal stability but also on primary and unstable thermal degradation products that are very important for investigation of thermal degradation mechanism [23].

In the present study, thermal characterization of polystyrene-*b*-poly(2vinyl pyridine), PS-*b*-P2VP, coordinated to Co, Cr and Au<sup>3+</sup> nanoparticles were investigated via DP-MS technique to elucidate the effect of metal coordination on thermal stability and degradation mechanism.

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## 2. Experimental

### 2.1. Materials and synthesis

PS-*b*-P2VP was purchased from Polymer Source Inc. (PS: Mn = 25,000, P2VP: Mn = 15,000, PDI = 1.04). Co<sub>2</sub>(CO)<sub>8</sub> and Cr(CO)<sub>6</sub> were purchased from Aldrich Chemical Company and HAuCl<sub>4</sub>·3H<sub>2</sub>O was purchased from Acros Organics and used without further purification. Toluene, purchased from Aldrich, was purified by refluxing over metallic sodium under nitrogen for two or three days.

Metal functional PMMA-*b*-P2VP polymers were prepared according to the literature methods [24]. As a summary, the polymer was dissolved in toluene by stirring overnight to form micelles. After the dissolution of the polymer, the metal or metal ion complexes, keeping the number of moles of metal or metal ion equal to that of 2VP repeating units, were added to this solution and refluxed for 8 h. After evaporation of the solvent under vacuum, the resultant product was analyzed by TEM, FTIR and DP-MS techniques. Among the several metals and metal ions tested nanoparticles could only be obtained for Co, Cr and Au<sup>3+</sup>.

### 2.2. Instrumentation

FTIR analyses of the samples were performed by Bruker Vertex 70 Spectrophotometer.

TEM imaging of the nanoparticles was carried out with a Tecnai G2 F30 instrument at 200 kV (UNAM – BILKENT University). The nanoparticles were dispersed on the carbon-coated copper grid from their diluted suspension in toluene.

Thermogravimetry analyses (TGA and DTA) were conducted on Perkin Elmer Pyris 1 TGA equipment, heating at 10 °C min<sup>-1</sup> under nitrogen atmosphere from ambient temperature to 600 °C.

Direct pyrolysis mass spectrometry, DP-MS, analyses were performed by a triple quadruple Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 10–1500 Da coupled to a direct insertion probe. During the pyrolysis, the temperature was increased to 50 °C at a rate of 5 °C min<sup>-1</sup>, then, was raised to 650 °C with a rate of 10 °C min<sup>-1</sup> and kept at 650 °C for 5 additional minutes. 0.01 mg samples were pyrolyzed in the flared quartz sample vials while recording 70 eV EI mass spectra at a mass scan rate of 1 scans<sup>-1</sup>. The analyses were repeated several times to ensure reproducibility. Each time, almost exactly the same trends were detected.

## 3. Results and discussion

The TEM images of the metal-functional polymers, Cr-PS-*b*-P2VP, Co-PS-*b*-P2VP, Au-PS-*b*-P2VP, shown in Fig. 1, pointed out well dispersed metal or metal ion nanoparticles in the PS-*b*-P2VP matrix. The size of Cr and Co nanoparticles were comparable, while

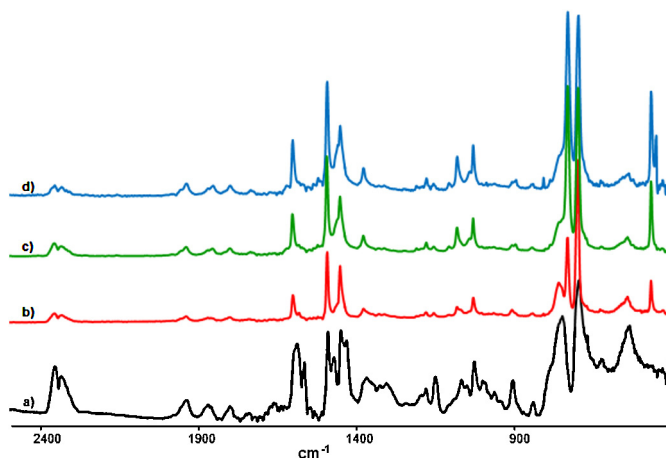


Fig. 2. FTIR spectra of (a) PS-*b*-P2VP, (b) Co, (c) Cr and (d) Au<sup>3+</sup> functional PS-*b*-P2VP.

Au(III) nanoparticles were about more than 2-folds smaller. Furthermore, the images indicated that coordination to Au<sup>3+</sup> was significantly more efficient. On the other, the extent of coordination to Cr seemed to be not very productive.

As the nanoparticle formation starts by the coordination of the electron-rich segment of the copolymer, 2-vinylpyridine, to the metal atom or ion by the exclusion of the ligands, the pyridine stretching and bending modes of pyridine ring are affected.

For Co and Cr functional PS-*b*-P2VP, the displacement of CO ligands by pyridines was confirmed by the disappearance of the peaks associated with carbonyl groups of Co<sub>2</sub>(CO)<sub>8</sub> (2023, 2041, 2071 cm<sup>-1</sup>) and Cr(CO)<sub>6</sub> (at around 2000 cm<sup>-1</sup>) completely. The relative intensities of the absorption peaks due to the pyridine stretching and bending modes in the range of 1590–600 cm<sup>-1</sup>, especially the ones at around 1590 cm<sup>-1</sup>, 1472 and 1431 cm<sup>-1</sup> were decreased significantly in all these complexes. Characteristic uncoordinated pyridine ring vibration at around 1590 cm<sup>-1</sup> shifted to 1604 cm<sup>-1</sup> for Co and Au<sup>3+</sup> functional copolymers and to 1602 cm<sup>-1</sup> Cr coordinated rings. A new absorption peak appeared at around 464 cm<sup>-1</sup> detected for all the composites was associated with N-metal stretching mode (Fig. 2). Considering the relative intensities of the peaks associated with N-metal stretching normalized with respect to the peaks due to phenyl ring vibrations it can be concluded that extent of coordination was comparable for Co and Au<sup>3+</sup> whereas not very fruitful for Cr in accordance with TEM results.

Pyrolysis of the metal and/or metal ion functional copolymers yielded almost identical thermal degradation products. Yet, inspection of pyrolysis mass spectra and single ion evolution profiles pointed out drastic changes in the relative intensities of P2VP based products, especially those associated with protonated oligomers of vinylpyridine, upon coordination to metal or metal ion.

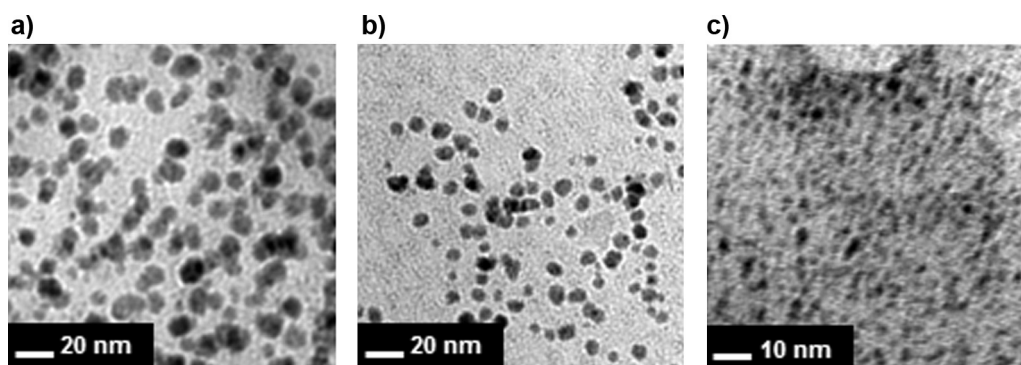


Fig. 1. TEM Images of (a) Co-PS-*b*-P2VP, (b) Cr-PS-*b*-P2VP and (c) Au-PS-*b*-P2VP.

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