Journal of Molecular Structure 1106 (2016) 479–484

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Doped copolymer of polyanthranilic acid and o-aminophenol (AA-co-OAP): Synthesis, spectral characterization and the use of the doped copolymer as precursor of α-Fe_2O_3 nanoparticles

Nasser Mohammed Hosny [a, *], Nourhan Nowesser [a], A.S. Al-Hussaini [a], Mohamed Shafick Zoromba [a, b]

[a] Chemistry Department, Faculty of Science, Port-Said University, 23 December Street, 42521, Port-Said, Egypt
[b] Department of Chemical and Materials Engineering, King Abdulaziz University, Rabigh, Saudi Arabia

ARTICLE INFO

Article history:
Received 24 June 2015
Received in revised form
12 August 2015
Accepted 30 October 2015
Available online 4 November 2015

Keywords:
Molecular precursor
Nanoparticles
Polymer
Optical materials

ABSTRACT

The copolymer of anthranilic acid and o-aminophenol (AA-co-OAP) was synthesized and characterized by IR, UV–Vis. and thermal analyses (TGA). Linear chain mode was suggested for the pure (AA-co-OAP). The effect of inclusion of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $FeCl_3$ on the spectral, thermal and optical properties of AA-co-OAP has been studied. Octahedral stereochemistry was suggested for Fe, Mn and Ni doped AA-co-OAP, while tetrahedral and square-planar geometries were suggested for Co and Cu doped AA-co-OAP, respectively.

Fe doped AA-co-OAP has been used as a precursor for α-Fe_2O_3 nanoparticles by thermal decomposition route at 800 °C. The obtained hematite has been characterized by XRD and TEM. The average size of the prepared nanoparticles was estimated as 34 nm. The optical band gap of the synthesized hematite nanoparticles was measured and compared with the bulk.

1. Introduction

Doping metal ions in the polymer matrix improves the properties of the polymers. The structural changes in the polymer matrix on doping appear as enhancement in the adsorption, thermal, photocatalytic, magnetic, electrical, optical, mechanical, and corrosion inhibition properties [1–6]. Doping inorganic nanoparticles to form polymer nanoparticle composites with characteristic features is the general trend [7], but the use of doped polymers as molecular precursor to synthesis metal oxides [8–10], or chalcogenides nanoparticles [11–13] is limited. It was found that, there is a relation between the size and the shape of the obtained nanoparticles and that of the molecular precursor [14]. The oxides nanoparticles obtained from molecular precursor synthesis have several advantages as, the oxides are highly pure with homogenous morphology, the method is environmental safe and can be used on large scale production [15–18].

Oxides of iron are important class of inorganic materials due to their wide applications in different processes, as cosmetics, paints, coating materials, catalysis, pollution treatments, opto-electronics devices, corrosion protection and chemotherapy [19–21]. The most common iron oxides are, the hexagonal structure hematite (α-Fe_2O_3), cubic structure maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4). Polyaniline has been used as a precursor for Fe_2O_3 nanoparticles [3]. To study whether, the substituents on the polyaniline backbone, will affect the phase and morphology of the produced Fe_2O_3 nanoparticles, the polymer (AA-co-OAP) has been selected to present these conditions. The polymer (AA-co-OAP) contains both hydroxyl and carboxyl groups as substituents. The hydroxyl group may bind to Fe^{3+} and the flexible carboxyl group can save good coating required for production of nanoparticles.

In this work, pure polyanthranilic acid-co-o-aminophenol (AA-co-OAP) and its doped form with $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $FeCl_3$ have been synthesized and spectrally characterized. The effect of inclusion of metal ions on the spectral, thermal, and optical properties of (AA-co-OAP) has been studied. The use of the Fe doped (AA-co-OAP) as precursor of α-Fe_2O_3 nano-particles has been discussed and the optical properties of hematite nanoparticles were reported.

* Corresponding author.
E-mail address: Nasserh56@yahoo.com (N.M. Hosny).

http://dx.doi.org/10.1016/j.molstruc.2015.10.103
0022-2860/

Table 1
IR spectra of AA-co-POAP and doped AA-co-POAP.

Copolymer	Mn doped	Fe doped	Co doped	Ni doped	Cu doped	Assignment
3400	3398	3405	3405	3405	3412	ν OH acid
3344	3304	3317	3303	3303	3276	ν OHphenolic
3203	3228	3189	3214	3228	3234	ν NH
1576	1587	1589	1593	1596	1590	ν C=N
1512	1539	1539	1532	1536	1549	ν C=C
1402	1402	1402	1402	1402	1402	δ C–OH
1211	1238	1211	1232	1238	1238	ν_s C–O
1149	1149	1155	1151	1144	1151	ν C–N
759	752	752	752	752	752	δ C–C

2. Experimental

2.1. Materials

Anthranilic acid, o-aminophenol and potassium dichromate were purchased from (Merck), hydrochloric acid and ammonia solution from (ADWIC).

2.2. Technique

IR spectra were recorded on a Mattson 5000 FTIR Spectrometer as KBr discs. Thermal analyses measurements (TG) were measured on a Schimadzu model 50 instrument by using alumina sample holder. The heating rate and nitrogen flow rate were 20 °C min^{-1}. and 20 cm^3 min^{-1}, respectively. UV2 Unicam UV/Vis. Spectrometer was used to measure the electronic spectra with 1 cm silica cell. XRD pattern was done by Philips XPERT-PRO using nickel filtered Cu Kα (λ = 1.5405 Å) radiation. CM 20 PHILIPS electron microscope was used to take TEM images.

2.3. Synthesis of doped polyanthranilic acid with $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $CuCl_2$

polyanthranilic acid o-aminophenol copolymer (AA-co-OAP) was prepared by *in situ* chemical oxidative polymerization. 3×10^{-2} mol anthranilic acid and 3×10^{-2} mol of o-aminophenol in 20 mL conc. HCl were mixed. The calculated amounts (3×10^{-2}) mol of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} chlorides in distilled water were gradually added to the reaction mixture with stirring. Then, 55 ml 1.0 M potassium dichromate (initiator) was added slowly to the reaction at the previous conditions for 45 min. The reaction was kept for 24 h at room temperature. 25 ml of ammonia solution (33% NH_4OH diluted by 25 ml distilled water) was added dropwisely until precipitation. The collected precipitates were filtered off, washed with distilled water, ethanol and dried in an electric oven at 70 °C for 5 h.

2.4. Synthesis of α-Fe_2O_3 nanoparticles

The Fe doped (AA-co-OAP) copolymer was calcined in a muffle furnace at 800 °C with a rate of 50 °C min^{-1} in air. Nanoparticles of α-Fe_2O_3 were obtained.

3. Results and discussion

The most important IR bands of the pure and doped copolymer (AA-co-OAP) are presented in Table 1 and Figs. S1 and S2.

Deprotonated poly(anthranilic acid-co-o-aminophenole) (AA-co-OAP) has been synthesized from anthranilic acid (AA) and o-aminophenol (OAP) in the absence and presence of metal ions by

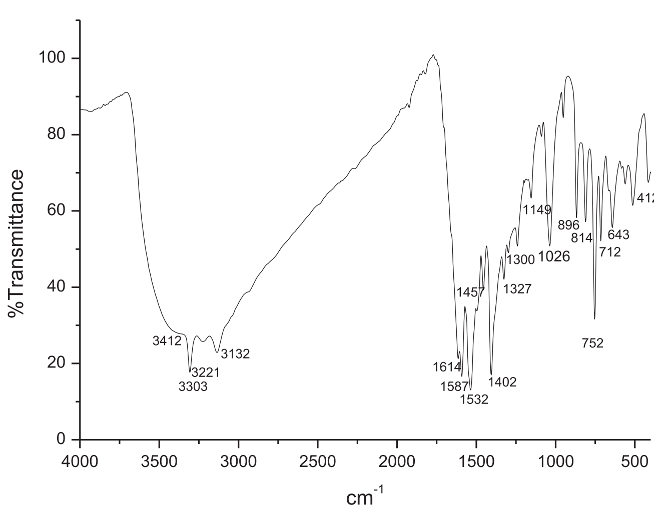

Fig. 1. IR spectrum of pure (AA-co-OAP).

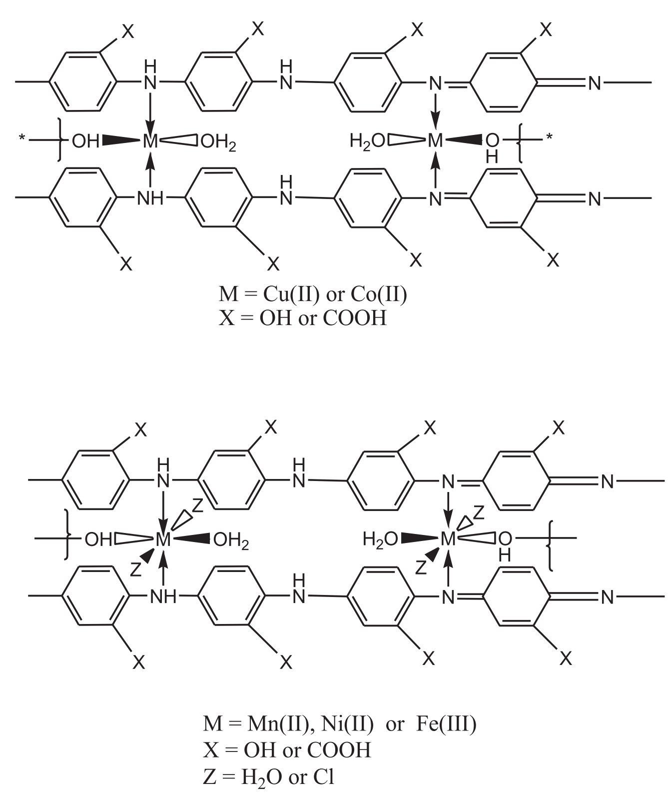

Fig. 2. Doped copolymer (AA-co-oAP) x = COOH or OH.