

The Synthesis of Poly(Hydroxamic Acid) and Its Metal Complexes

S. Hossein Hosseini and Ali Akbar Entezami

Polymer Chemistry Laboratory, Faculty of Chemistry, Tabriz University, Tabriz, I.R.Iran

Received: 21 June 1994; accepted 26 November 1994

ABSTRACT

Acrylcarbohydroxamic acid is synthesized, purified by azeotropic co-evaporation technique, and polymerized, under free radical condition. The complexes of poly(hydroxamic acid) with certain ions: Fe^{+3} , Cr^{+3} , Rh^{+3} , Ir^{+3} , Al^{+3} , Cu^{+2} , Pd^{+2} , Ni^{+2} , Pt^{+2} , Co^{+2} , at different pH are reported.

Key Words

poly(hydroxamic acid), acrylcarbohydroxamic acid, radical polymerization, polymer-metal complex.

INTRODUCTION

The hydroxamic acid derivatives and their polymers are synthesized for a variety of purposes and are widely used in the medical, industrial, pharmaceutical, agricultural and textile fields. These compounds are a primary material for synthesis of some drugs such as antitumor drugs, antibiotics and enzyme activity inhibitors [1].

Hydroxamic acid derivatives and their polymers have long been known for their special ability to form complexes with heavy metals, particularly Fe(III), Cu(II) [2].

PHA can be used to measure many elements quantitatively in chromatography and for separation of various ions in biological and

sensitive solutions [3].

Poly(hydroxamic acid) was synthesized via polyacrylamide [4], polyacrylic acid [5] and polyacrylonitrile [6] at different conditions.

The poly(hydroxamic acid) obtained possessed 70% maximum hydroxamic acid groups. The poly(hydroxamic acid) prepared by our procedure contains 100% of hydroxamic acid groups.

EXPERIMENTAL

Materials

Acrylamide (Fluka AG, Buchs SG), was recrystallized twice from methanol (Analytical

Reagent grade) and dried in vacuum over silica gel for a week.

Ethyl acrylate (Merck-Gehalt. GC, >99%), washed repeatedly with aqueous NaOH until free from inhibitors such as hydroquinone, then washed with saturated aqueous CaCl₂ and distilled under reduced pressure.

Acrylic acid (Merck-Gehalt, 99%), purified by vacuum distillation through a column packed with copper gauze to inhibit polymerization.

Hydroxylamine-hydrochloride (Fluka AG, CH-9470, Buchs) used as purchased.

Instrumentation

GC Mass Spectrometer QP100 Shimadzu; Philips Analytical PU9600 FTIR Spectrometer; Osmomat 030 Gonolcc

Preparation of Acrylcarbohydroxamic Acid

To the appropriate vinyl compounds (ethyl-acrylate, acrylamide, acrylic acid) (0.05 mol) and hydroxylamine hydrochloride (13.9g, 0.2 mol) dissolved in 80 mL methanol, 50 mL KOH (5M) are added dropwise with stirring. After stirring for 36 hours at room temperature methanol is evaporated and the solid residue is acidified with acetic acid/water (50:50; 50 mL) and extracted with ethyl acetate (3x50 mL). The concentration of organic phases affords an oil, which after azeotropic co-evaporation with toluene (2x20 mL) and then with ethanol (2x20 mL), afforded a solid. Washing with ether (10 mL) gave acrylcarbohydroxamic acid (yield, 45-82%), mp= 87 °C, UV: λ_{max} = 207 nm in acetonitrile, FTIR: 3450, 1690, 1600, 1020 cm⁻¹, mass spectrum: (20, 70 eV) m/e= 87.

Preparation of Poly(Hydroxamic Acid) (PHA)

PHA was prepared by polymerizing a solution of acrylcarbohydroxamic acid (95: 5 v/v) water/DMF with azobisisobutyronitrile in N₂ atmosphere at 60°C and after 30 minutes the polymer thus produced precipitated in ice methanol. FTIR: 3435, 2983, 1628, 1406 1030 cm⁻¹.

Elemental analysis (Calculated): %C: 41.49, %H: 5.75 %N: 16.09 %O: 36.78.

(Found): %C: 42.22, %H:5.76, %N:15.68, %O: 36.3.

Preparation of Metal Complexes

PHA - Fe (III)

-To a solution of FeCl₃. 6H₂O(0.2 mmol) in 2mL of H₂SO₄ (4M), a solution of PHA (0.1 g) in 25 mL of H₂O was added dropwise while stirred rapidly.

The reaction mixture was stirred for 12 hours at room temperature and then the dark-brown solid was washed with several portions of hot water.

-Anhydrous ferric chloride (0.191 g, 0.17 mmol) was added to a rapidly stirred solution of PHA(0.1g) in 50 mL of THF containing a few milliliters of pyridine. The burgundy colored solution was stirred at room temperature for 5 hours, and then concentrated to dryness in vacuo. The dark-brown solid was washed with hot water.

PHA- Cr (III)

-A solution of Cr (NO₃)₃. 9H₂O (3.2g, 8 mmol) in 30 mL of H₂O was added to a rapidly stirred solution of potassium poly(hydroxamate) (0.1 g) in 150 mL of H₂O. The resulting green slurry was stirred for 12 hours at room temperature and suction filtered. The blue-green solid was washed well with H₂O and ethyl ether.

-To a solution of Cr(NO₃)₃.9H₂O (0.4 g, 1.0 mmol) in 2 mL of H₂O was added a solution of PHA(0.1g) in 60 mL of buffer pH= 4.7 (0.1N NaOAc-HOAc). The reaction mixture was stirred for 12 hours at room temperature, filtered, and further treated as described above.

PHA-Ir (III)

(NH₄)₃ IrCl₆ (1mmol) was dissolved in H₂O (5 mL) and sodium acetate (0.9 mmol) in H₂O (30 mL) was then added. Ethanol was added to the point of almost precipitating ionic products. PHA (0.1g) was dissolved in 10 mL ethanol and the mixture was heated to 50°C for 2 hours, cooled and stirred for a further 3 days at 20°C. The red precipitate

was collected, washed with water, and dried at room temperature.

PHA-Rh (III)

Rhodium trichloride (1mmol) was dissolved in ethanol (10 mL). Sodium acetate (1mmol) in H₂O (5mL) and EtOH (5 mL) was added to this solution, and the mixture was filtered. PHA (0.1 g) in ethanol (20 mL) was added to the mixture and the resulting solution was heated almost to the boiling point for 10 minutes. On cooling, the solution was decanted from the blue product which was washed with ethanol.

PHA-Al(III)

Aluminium hydroxide was freshly prepared from Al (NO₃)₃.9H₂O using diluted NaOH. The resulting gel was washed twice with H₂O and filtered. The excess of hydroxide was mixed with 0.1 g of PHA in warm H₂O. The excess of Al(OH)₃ was removed of the aluminium complex and evaporated to dryness. The violet aluminium complex obtained was washed in hot water and ethanol.

PHA-Ni(II)

A typical procedure is given for Nickel-PHA. PHA (0.1g) dissolved in 20 mL of water was added to NiCl₂.6H₂O(0.5mmol) in 10 mL of water and the pH raised to 8.3 with NaOH. The green precipitate which results was filtered and washed with hot water and ethanol.

PHA-Co (II)

-To an aqueous mixture of freshly prepared Co(OH)₃ was added an excess of PHA(0.1g) and stirred for 12 hours at room temperature, then the pink cobalt (II) complex was obtained.
-Oxygen was bubbled through an ethanolic solution of CoCl₂ and an excess of potassium poly (hydroxamate) for 12 hours at room temperature. Pink cobalt(II) complex was isolated and washed with hot water and ethanol [7].

PHA-Pt(II)

A solution of K₂PtCl₄ (0.305 g, 0.735 mmol) in 10 mL of H₂O was added dropwise to a rapidly stirred

solution of PHA(0.1g) in 5mL of acetone. The reaction mixture was heated for 15 minutes at 55 °C, stirred for 12 hours at room temperature and heated again for 3 hours at 55 °C. After the mixture was cooled, resulting yellow precipitate was filtered and then washed with hot water.

PHA-Pd(II)

-A solution of PdCl₂ (66.2 mg, 0.373mmol) in 500 mL of phosphate buffer pH=6.0(0.1M) was added slowly to a stirred solution of PHA (0.1g) in 30 mL of the same buffers. The brown solution was stirred for 2 days at room temperature and then concentrated to dryness in vacuo. The red solid was washed with several portions of hot water.

-A solution of PHA(0.1g) in a few milliliters of ethanol-water (50:50 v/v) was added dropwise to a rapidly stirred solution of PdCl₂ (88.4 mg, 0.499 mmol) in 10 mL of 1N HCl. The resulting deep red solution was stirred for 4 hours at room temperature and then adjusted to pH=7 with solid NaHCO₃. The resulting red precipitate was filtered and then washed with hot water and red crystals were obtained.

PHA-Cu(II)

PHA(0.1 g) dissolved in 20 mL of water was added to CuCl₂. 2H₂O (0.5 mmol) in 10 mL of water and the pH regulated to 5.5 with H₂SO₄ (2M). The resulting dark-green precipitate was filtered and washed with hot water and ethanol.

RESULTS AND DISCUSSION

Acrylcarboxhydroxamic acid (AHA) was synthesized by reaction of the corresponding vinylic compounds such as, acrylamide, acrylic acid, and ethyl acrylate with hydroxylamine hydrochloride in the basic media (Table 1).

The PHA was prepared by free radical polymerization of AHA with AIBN at 60 °C under N₂ atmosphere and DMF as solvent. The resulting polymer was precipitated with ice methanol. The fractionation of polymer was accomplished by the triangular method. The PHA was dissolved in

CONCLUSION

Poly(hydroxamic acid) synthesized through acrylcarbohydroxamic acid contains 100% hydroxamic acid groups. As a result a high degree of complexation with metal ions can be obtained.

REFERENCES

- 1 Ibarra, I.; Kehl, H; *IRCS Med. Sci.* **13**, 579 (1985).
- 2 Bass, V.C.; Yoc, J.H; *Talanta*, **13**, 735 (1966).
- 3 Baya, C.A.; Simunic, J.L.; *Inorg. Chem.* **29**, 1090-1092 (1990).
- 4 Domb, A.J.; *J. Poly. Sci. Part A, Poly. Chem.* **26**, 2623-2630 (1988).
- 5 Hoffman, Robert, K.; U.S. 6PP, CA112 (A); 588302 (1989)
- 6 Zvere, M.P.; Barash, A.N.; Ger. Offen, 4PP (1988).
- 7 Leong, J.; Raymond, K.N.; *J.Amer. Chem. Soc.* **96**: 6, 1757-1762 (1974).
- 8 Koshy, V.C.; Tandon, S.G.; *Nat.Acad.Sci.Letters*, **5**, No10(1982).
- 9 Pass, G.; Sutcliffe, H.; *Practical Inorg. Chemistry*, Chapman & Hall, London 1968..