European Polymer Journal 44 (2008) 2330–2338

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Aminodiacetic water-soluble polymer–metal ion interactions

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ARTICLE INFO

Article history:
Received 16 January 2008
Received in revised form 9 April 2008
Accepted 8 May 2008
Available online 13 May 2008

Keywords:
Glycidyl methacrylate-iminodiacetate
Water-soluble polymer
Polychelatogen
Antibacterial activity

ABSTRACT

The retention properties for metal ions, the maximum retention capacity, the antibacterial and mutagenic activity of water-soluble metal ion complexes from water-soluble poly[2-hydroxy-(3-methacryloyloxypropyl)aminodiacetic acid] P(HMPADA) were studied. HMPADA was synthesized by radical polymerization in aqueous solution. The water-soluble polymer (WSP) P(HMPADA), containing ester, hydroxy, tertiary amine, and two carboxylic acid groups in every monomeric unit was investigated as polychelatogen in view of its potential metal ion binding properties using the liquid-phase polymer based retention (LPR) technique under different experimental conditions. The water-soluble complexes were investigated as biocides. Metal ions investigated at pH 3, 5, and 7 were: Ag^{+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+}. Depending on pH, P(HMPADA) showed a different interaction affinity, where the highest interaction occurred at pH 7. Polymer–metal ion interaction showed the following affinity order: tri-valent >di-valent >mono-valent ion. Maximum retention capacity (MRC) ranged between 17.2 and 342.2 mg metal ion/g polymer for Cu^{2+} and Ag^{+}, respectively. FT-IR showed a variation in $\nu C{=}O$, $\nu O{-}C{=}O$, νOH absorption signals, and Far-IR showed new signals corresponding to metal–O and metal–N interaction, indicating a participation of carboxylic acid, amine, and hydroxy groups of polymer–metal ion complexes. Antibacterial activity of Ag^{+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} complexes were studied. These complexes presented a higher biocide activity against *Staphylococcus aureus* (Gram-positive) than for *Escherichia coli* (Gram-negative) with a lowest minimum inhibitory concentration (MIC) of 4 mg/mL for polymer-Cd^{2+} complex. Scanning electron microscopy (SEM) showed the interaction between polymer–metal ion complexes and bacteria surface. All samples showed low genotoxic activity.

1. Introduction

Metal ion removal from dilute water solutions is a fundamental step in water treatment. The liquid-phase polymer-assisted retention (LPR) has demonstrated to be an efficient tool to remove metal ions from dilute solutions [1–10], although it is absolutely necessary to have a polymer that is chemically suitable to the acid conditions and metal ions concentrations in order to avoid gelification or precipitation processes. Furthermore, this technique can be used to obtain water-soluble polymer–metal ion complexes that have emerged as a new generation of materials with tremendous potential in fields such as superconducting materials, ultra-high strength material, liquid crystals, catalysts, and biocompatible polymers [11–14]. Different acid polymers have demonstrated good efficiency for this purpose, such as: poly(acrylic acid), P(AA), poly(methacrylic acid), P(MAA), poly(2-acrylamido glycolic acid), P(AGA), poly(vinyl sulfonic acid), P(VSA), poly(styrene sulfonic acid), P(SSA), and poly(2-acrylamido-2-methyl propane sulfonic acid), P(APSA). All these polymers, except P(AGA) and P(APSA), have only one coordinating or exchangeable group in every monomeric unit. Polymer functionalization or new functional polymer synthesis can be used to modify the interaction pattern or increase the maximum retention in

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doi:10.1016/j.eurpolymj.2008.05.001

comparison with the homopolymers. Glycidyl methacrylate (GMA) has been employed with success to synthesize new monomers or modify existing polymers [15–16], and its structural modification with sodium imidoacetate (Na-IDA) resulted in a water-soluble polymer with several functional groups. In this sense, Furusaki et al. introduced a high density of iminodiacetate groups in polyethylene's hollow-fibber membrane to increase the Cu^{2+} interaction [17–19]. Subsequently, Chen studied P(HMPADA) or P(GMA-IDA) as wastewater treatments for metal ion interaction with Cr^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} from water-insoluble polymer using *N,N′*-methylene-bis-acrylamide as cross-linking reagent; with, he studied the stability constant complexes of from poly(styrene-co-GMA-IDA) with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. He made also fibers from poly(propylene-graft-GMA-IDA)-Ag^{+} and determined the conductivity of poly(ethylenglycol-methylethermethacrylate-co-GMA-IDA)-Li^{2+} [20–22]. P(HMPADA)-Fe^{3+} cross-linked with 1,4-divinylbenzene has been used to increases the content of phospho peptides from peptide mixtures to study phosphorylation of proteins [23].

It is well known that poly anions do not have antibacterial activity, and metal ions such as Ag^{+}, Cu^{2+}, and Zn^{2+} have high antibacterial activity and low toxicity. With this concept, water-insoluble complexes [24–26] from natural and synthetic polymers have been developed to study its antimicrobial properties.

The goal of the present manuscript is to study the metal ion retention capability of poly[2-hydroxy-(3-methacryloyloxypropyl)aminodiaceticacid] and the potential biocide activity for *Escherichia coli* and *Staphylococcus* aureus as well as to determine the genotoxic activity of the polymer and polymer–metal complexes with Ag^{+}, Cu^{2+}, and Zn^{2+}.

2. Experimental part

2.1. Reagents

Glycidyl methacrylate (GMA), 96%, Aldrich Co., FW: 163.13 g/mol; sodium iminodiacetate (IDA) were used without further purification. Ammonium persulfate (AP, Fluka) was used without further purification. Metal standard solutions of 1000 ppm (Merck). $Al(NO_3)_3 \times 9H_2O$, 98.5%, p.a. Merck; $Cr(NO_3)_3$ $9H_2O$, 98%, p.a. Merck; $Fe(NO_3)_3$ from a 1000 ppm solution, Merck; $Co(NO_3)_2 \times 6H_2O$, 99%, p.a. Merck; $Ni(NO_3)_2 \times 6H_2O$, 99%, p.a. Merck; $Cu(NO_3)_2 \times 3H_2O$, 99%, p.a. Merck; $Zn(NO_3)_2 \times 6H_2O$, extra pure, Merck; $AgNO_3$, 99.8%, p.a. Merck; $Cd(NO_3)_2 \times 4\ H_2O$, 99%, p.a. Merck; $Pb(NO_3)_2$, 99%, p.a. Merck. Sodium hydroxide (NaOH, Merck), nitric acid 70% (HNO_3, Caledon).

2.2. Polymer synthesis

To obtain poly[sodium 2-hydroxy-(3-methacryloyloxypropyl)amino diacetate], P(HMPADA-Na), a 0.4 M solution of glycidyl methacrylate (5.86 g/100 mL of GMA) and 0.4 M of sodium iminodiacetate (7.23 g/100 mL of IDA-Na) were added to a round three-necks flask. After 24 h at 60 °C of stirring, a clear yellow solution was obtained corresponding to HMPADA-Na (see Scheme 1). The monomer was polymerized in a polymerization flask by adding 1 mol% (0.44 mmol) of ammonium persulfate under N_2 (g) atmosphere. The polymerization flask reaction was placed in an oil bath at 70 °C for 24 h.

2.3. Polymer purification

The polymer was purified and fractionated through ultrafiltration membranes with molecular mass cut offs (MMCO) of 10,000, 30,000, and 100,000 Da, using 0.01 M HNO_3 as solvent, to obtain the acidic polymer. Fractions lower than that 10,000 Da were discarded, and polymers from the fractions higher than that 10,000 Da were lyophilized obtaining polymer fractions with different molecular weights.

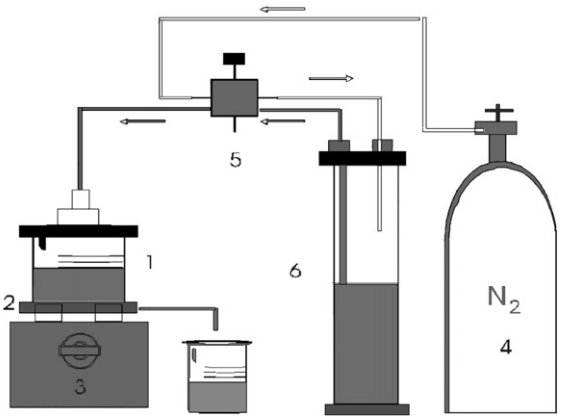
2.4. Polymer characterization

After polymer purification, a fraction higher than 100,000 Da was characterized by FT-IR (in KBr), ^{1}H NMR, and ^{13}C NMR (using deuterium oxide as solvent and tetramethylsilane as reference for 0.0 ppm) spectroscopy. Polymer was previously characterized [14].

2.5. Metal ion retention by LPR technique (washing method)

To ensure a high level of ligand sites, the copolymer repeat unit: metal ion ratio (in mol) was 40: 1. Then, 20.0 mL of a solution containing 1.0×10^{-2} mmol/L of a water-soluble homopolymer (0.1160 g of fraction >100,000 Da) and 2.5×10^{-4} M of metal ions (5 mmol of each metal ion or 5 meq, 10 meq and 15 meq for mono-, di- and tri-valent metal ion, respectively) are placed into the solution cell provided with a ultrafiltration, membrane with a molecular mass cut off (MMCO) of 10,000 Da (Millipore, Amicon). Pb^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+} metal ions were studied at pH 3.0 and 5.0 to avoid the precipitation of hydroxy species, and Ag^{+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} were studied at pH 3.0, 5.0 and 7.0. All metal ions were added as a mixture into the ultrafiltration cell.

The pH was adjusted with dilute HNO_3 and NaOH. A washing solution (water at pH = 3.0, 5.0, and 7.0,



Scheme 1.