



# Synthesis and characterization of an insoluble polymer based on polyamidoamine: Applications for the decontamination of metals in aqueous systems



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## ABSTRACT

We present a novel, insoluble, low-generation polyamidoamine (PAMAM)-based polymer. The monomer and polymer were characterized by fourier transform infrared spectroscopy, electrospray ionization mass spectrometry and thermogravimetric measurement, revealing that G0 acryloyl-terminated PAMAM were synthesized and polymerized using ammonium persulfate as an initiator, producing a high-density PAMAM derivative (PAMAM-HD). PAMAM-HD was tested for its ability to remove Na(I), K(I), Ca(II), Mg(II), Cu(II), Mn(II), Cd(II), Pb(II) and Zn(II) ions from acidic, neutral and basic aqueous solutions. PAMAM-HD efficiently removed metals ions from all three solutions. The greatest absorption efficiency at neutral pH was observed against Cu(II), Cd(II) and Pb(II), and the experimental data were supported by the calculated  $K_d$  values. Our data could have a significant impact on water purification by providing an inexpensive and efficient polymer for the removal of metal ions.

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## 1. Introduction

Most heavy metals in the environment originate from industrial processes, including automobile emissions, mining, battery manufacturing, fossil fuels, metal plating, and the electronics industry (Guilherme et al., 2007). Many technologies can be used to remove heavy metal ions, including ion exchange chromatography, alkaline precipitation, electrochemical extraction, membrane retention and filtration (Akpoy and Muchie, 2010). However, these methods suffer from drawbacks such as the production of solid residues, poor selectivity, relatively low loading capacities and the release of dangerous ionic metals and/or organic compounds.

These challenges have been addressed by the development of a promising novel insoluble polymer based on a modified low-generation form of polyamidoamine (PAMAM). Specifically, PAMAM dendrimers have the ability to chelate metal ions from solutions (Tomalia et al., 1985). This attribute has primarily been exploited to synthesize metal nanoparticles (Huang et al., 2008; Witham et al., 2010; Li et al., 2011), but dendrimer based chelation has recently attracted interest. Chelation is a low-cost and environmentally-friendly technique that has the potential to overcome the limitations of other removal strategies (Reed, 2001; Roundhill, 2004). Many materials have been used for chelation, including polymers, activated carbon, metal oxides, silica, and ion exchange resins (Duran et al., 2008; Cavus and Gurdag, 2008; Copello et al., 2008; Uguzdogan et al., 2009). Studies with PAMAM dendrimers and derivatives have provided excellent preliminary results (Gugliotta et al., 2010; Rether and Schuster, 2003; Zhang et al., 2013; Li et al., 2011).

PAMAM is commercial dendrimer that was synthesized and investigated for the first time by Tomalia et al., (1985). Dendrimers

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are macromolecules that have recently generated a great deal of interest, reflecting their potential as templates for the controlled fabrication of nanosized metal particles that can be used for catalysis and to create electronic devices with specific functions that take advantage of their energy-harvesting and light-emitting properties (Laurent and Caminade, 2011; Kumar et al., 2012; Lo et al., 2009). Such dendrimers consist of globular macromolecules with three covalently-bonded components: an ethylenediamine core, interior branch units, and terminal branch units. The nanocavities and straightforward functionalization of terminal groups offer unique characteristics in a wide range of applications, such as drug delivery (Zhu and Shi, 2013), biomedical engineering (Rajasekhar and Liao, 2012), gene therapy (Santander-Ortega et al., 2012), catalysis (Myers et al., 2011), biosensing (Sarkar Abhijit Kaganove et al., 2005), water purification (Rether and Schuster, 2003; Zhang et al., 2013) photonics and electronics (Astruc et al., 2010).

Here we describe the synthesis of a novel, low-cost polymer based on PAMAM G0 using simple organic transformations, and the quantitative evaluation of its ability to remove metal ions from water. We also carried out calculations to study the energetics and structural properties of metal complexes, which supported our empirical analysis of complex formation and confirmed that multiple factors in addition to electronic and electrostatic interactions must be considered to achieve better predictions.

## 2. Materials and methods

### 2.1. Reagents

All reactions were carried out under an inert nitrogen atmosphere. Ethylenediamine (EDA), methyl acrylate (MA), triethylamine (TEA), acryloyl chloride and ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) were obtained from Sigma–Aldrich. All other reagents were used without further purification. Anhydrous acetone, N,N-dimethylmethanamide (DMF), toluene, diethyl ether and methanol were supplied by Merck.

### 2.2. Synthesis and characterization of low-generation polyamidoamine dendrimers

Low-generation PAMAM dendrimers, specifically generation G0, were synthesized in a two-step process involving the Michael

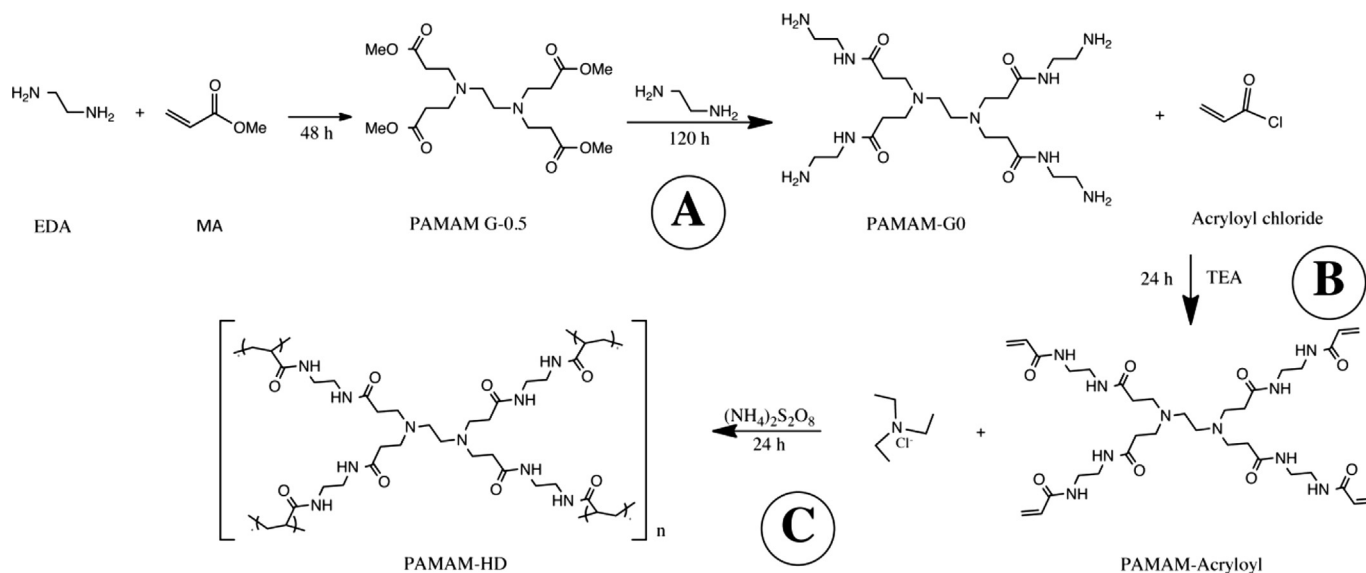
addition of a suitable amine initiator core with MA, and exhaustive amidation of the resulting esters with large excess of EDA, as reported previously (Tomalia et al., 1985). This strategy for the preparation of dendrimers is known as the divergent synthesis method. The details of PAMAM G0 synthesis and characterizations are described in Text S1 in the SI.

### 2.3. Synthesis and characterization of acryloyl-terminated PAMAM G0 (PAMAM-acryloyl)

PAMAM-acryloyl used for the syntheses of PAMAM-HD was generated by the nucleophilic substitution of the amines with acryloyl chloride as described in Scheme 1B (Uguzdogan and Kabasakal, 2010). PAMAM G0 obtained as described above ( $3.87 \times 10^{-5}$  mol) was dissolved in 5.0 mL DMF in the presence of TEA (21.59  $\mu$ L) and cooled in an ice bath. Freshly distilled acryloyl chloride (12.53  $\mu$ L) was added dropwise to the above solution while stirring. The reaction mixture was brought to room temperature and stirred overnight before pouring into a large excess of diethyl ether. The precipitated PAMAM-acryloyl was separated, rotoevaporated to remove the residual diethyl ether and dried under vacuum until the weight was constant (yield <90%). The PAMAM-acryloyl monomer was characterized by FT-IR, TGA and ESI-MS.

### 2.4. Synthesis of PAMAM-HD

The PAMAM-acryloyl monomer was cross-polymerized using the solution polymerization method as follows. Initially, the monomer and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were dissolved in water in a Pyrex glass flask at concentrations of 1.0 and 0.01 mol/L, respectively. Prior to polymerization, oxygen was removed by purging with nitrogen for 10 min and the Pyrex glass flask was sealed. Then the reactor was placed into a shaking water bath equipped with a temperature control system at room temperature. The water bath was heated to 60 °C in 30 min and incubated for 12 h shaking at 120 cpm. The precipitated PAMAM-HD was washed several times with water to eliminate unreacted initiator and inorganic byproducts, lyophilized to eliminate the water until the weight was constant. The polymerization of PAMAM-HD is described in Scheme 1C. PAMAM-HD is insoluble in organic solvents, thus only FT-IR and TGA were used to characterize the product.



Scheme 1. Synthesis of PAMAM-HD.

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