



# Is the aquatic toxicity of cationic polyelectrolytes predictable from selected physical properties?

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## HIGHLIGHTS

- Cationic acrylamide polyelectrolytes (cPAMs) can be harmful to the aquatic biota.
- Molecular weight, charge density and intrinsic viscosity of cPAMs agree as expected.
- CPAM's toxicity depends on physical properties but trends are species-specific.
- Bacteria and macrophytes were the least sensitive to cPAMs due to uptake constraints.
- The toxic response of the most sensitive test species should assist cPAMs design.

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## ABSTRACT

Cationic acrylamide-based polyelectrolytes (cPAM) are widely used in industry. They can be designed for optimal performance in a specific application, but this opportunity means the environmental safety of all different alternatives needs to be addressed. Both the inclusion of environmental toxicity as a design variable and the establishment of relationships between structure and ecotoxicity are thus current challenges. The aim of this study was to assess whether structural variables such as molecular weight, charge density and the integrative intrinsic viscosity parameter can be used to predict the environmental safety of cPAMs, as well as if these relationships are stable when the biological models change. Five cPAMs comprising molecular weight and charge density gradients were tested against bacteria, microalgae, macrophytes and daphnids. While correlations were found between physical properties of cPAMs as expected, no clear ecotoxicity patterns could be identified. All cPAMs can be classified as harmful to aquatic life on the basis of the responses elicited in the most sensitive organisms, microalgae and daphnids. Unicellular bacteria were the least sensitive eco-receptors possibly due to cell wall structure or the protective effect of the ionic strength of the test medium. The macrophytes were also tolerant to cPAMs exposure, which may be related to exposure avoidance mechanisms. The order of toxicity of cPAMs depended on the test organism, preventing the establishment of stable structure-ecotoxicity relationships. Therefore, the study leads to the overall generalist recommendation of relying on the most sensitively responding test organisms when developing new (eco)safe-by-design cPAMs.

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## 1. Introduction

Polyelectrolytes are water-soluble polymers of high ionic group content. They have been used worldwide in flocculation processes

as alternatives or complementary to more traditional approaches mostly using inorganic coagulants such as alum (Bolto and Gregory, 2007). These polymers are of high molar mass order ( $10^6$ – $10^7$  g/mol), bearing positive or negative charges (more than 15% ionic groups) either on the side-chain groups or on the backbone (Rabiee et al., 2015). Cationic acrylamide-based polyelectrolytes are the most preferred for a broad field of applications, including in wastewater treatment, mineral processing, pulp and papermaking,

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food processing, personal care product's manufacturing, and controlled drug release technologies (reviewed by Rabiee et al., 2015). Such a variety of applications results from the suitability of polyelectrolytes to be specifically tailored towards enhanced functionality by manipulating key features, i.e. charge density, molecular weight and chain architecture (Rasteiro et al., 2011, 2010). For example, flocculation activity is dependent on the conformation of the polyelectrolyte as adsorbed to the target particle, which is determined by concentration, but also by the interplay of its molar mass, charge density and degree of molecular branching (Antunes et al., 2010; Biggs et al., 2000; Bremmell et al., 1998).

All the options for fine-tuning polyelectrolyte functionality ultimately translate into endless lists of alternative compounds. This is obviously a great achievement from the technological and target-specificity point of view, but poses also significant problems when it comes to characterize a wide range of alternatives for e.g. licencing purposes. An important part of this process is the characterisation of the environmental compatibility of the new chemicals as required by regulatory agencies worldwide (e.g. REACH Directive; EC, 2006). In general, polymers are exempt from registration and evaluation under REACH unless its hazardous potential to human and environmental health has been proven or until further decision on which ones should be registered. The reason for exemption relies on their high molecular weight and consequently low likelihood of biological reactivity (ECHA, 2012; Polymer REACH, 2011). However, monomers and other reactants are covered by the registration and evaluation requirements (Polymer REACH, 2011), and polymers are not exempt from specific safety regulation such as the European CLP directive (EC 1272/2008 on classification, labelling and packaging of substances and mixtures). Acrylamide, the major monomer of the cationic polyelectrolytes addressed in the present study, has been proven to hold carcinogenic and mutagenic properties. As a result, it has been classified as a substance of very high concern included in the list of candidates requiring authorization following detailed environmental and human health risk assessment (ECB, 2002; Smith and Oehme, 1991).

The widespread (over)use of flocculants mostly in wastewater treatment has been leading to their significant discharge in the environment (Harford et al., 2011; Liber et al., 2005; Swift et al., 2015), but their ecotoxicological properties have been poorly addressed (Harford et al., 2011; Liber et al., 2005). Although the common assumption that adsorption phenomena can mitigate polyelectrolyte toxicity (Bolto and Gregory, 2007; Cary et al., 1987; Goodrich et al., 1991; Hamilton et al., 1994), there is evidence of hazardous potential of these compounds towards the aquatic biota under particular conditions of overdosing, accidental release and/or release in an unbounded state (ARC, 2012; De Rosemond and Liber, 2004; Liber et al., 2005; Rowland et al., 2000). The ecotoxicity of polyelectrolytes to freshwater species varies widely, with median effect concentrations ranging between 0.04 and more than 4000 mg/L, depending on ionic state and tested organisms (ARC, 2012). This wide variation makes it difficult to draw assumptions on the overall safety of these chemicals.

The need for including environmental toxicity as a variable in the design and early development of cationic polyelectrolytes becomes apparent from the rationale above. This need has already been emphasized some time ago by Hamilton et al. (1994), who also argued that structure-activity(toxicity) relationships (SARs) are useful in this context given the large range of options technically available to manipulate the molecular architecture of these compounds. Furthermore, and considering the possibility of future additional requirements in the registration of new polyelectrolytes regarding their environmental safety, research on SARs would be a key asset to improve read-across (or data gap filling) frameworks

for this category of chemicals (for the basics on this regulatory approach, see e.g. ECHA, 2015; Williams et al., 2011). Although SARs have been developed recently for polyelectrolytes, such advances relate specifically to a renewed interest in their biomedical uses (Ji et al., 2011; Tejero et al., 2015a, 2015b; Timofeeva et al., 2015). Ecotoxicity has been largely unexplored as a meaningful component of cationic polyelectrolyte SARs. Still, scattered studies exist denoting the effects of polymer chemistry, molecular weight, charge density and chain architecture (Costa et al., 2014; Goodrich et al., 1991; Hall and Miranda, 1991) on the ecotoxicity of cationic polyelectrolytes.

In the present study, a series of five cationic acrylamide/acryloyloxyethyltrimethyl ammonium chloride copolymer polyelectrolytes, comprising molecular weight and charge density gradients, was investigated. Their ecotoxicity was assessed through tests with bacteria, green microalgae, macrophytes and cladocerans. This set of biological models covers key functional groups within aquatic ecosystems. Importantly, it also includes different cell types and polyelectrolyte uptake routes, which may affect the magnitude of possible toxic effects. The overarching aim of this study is two-fold. First, the study intends to establish relationships between structural variables and the ecotoxicity of cationic acrylamide polyelectrolytes. The role played by molecular weight and charge density was central, but a relationship between ecotoxicity and intrinsic viscosity was also hypothesized based on previous studies (Costa et al., 2014). In practice, intrinsic viscosity is a parameter aggregating several polymer properties (Rasteiro et al., 2010). Secondly, the study aimed to elucidate whether possible structure-ecotoxicity relationships would be stable as the targeted biological model changes (see Santos et al., 2015) since knowing these inconsistencies is crucial to incorporate environmental safety variables in the rational design of chemicals in general, and in polymers such as polyelectrolytes in particular.

## 2. Material and methods

### 2.1. Polyelectrolytes characterisation

Five cationic polyacrylamides (cPAM) with different molar mass and charge density were used in this study. They all are copolymers of acrylamide and acryloyloxyethyltrimethyl ammonium chloride with a cationic monomer content between 40 and 50% (w/w), developed and supplied by AQUA-TECH, Switzerland (Hernandez-Barajas et al., 2003a, 2003b, 2001). They were synthesised by inverse-emulsion polymerisation as described in detail elsewhere (Barajas et al., 2004; Palomino et al., 2012; Rasteiro et al., 2010). The cPAMs were coded according to their expected charge density ( $E > F$ ) as indicated by the manufacturer; and molecular weight (1–3), which was confirmed as described below.

#### 2.1.1. Chain size distribution and molecular weight measurements

Distribution of polymer chain size, expressed in equivalent spherical diameters (hydrodynamic diameters;  $d$ ), and molecular weights (Mw) were determined by dynamic light scattering and static light scattering, respectively (Zetasizer Nano ZS, ZEN3600, Malvern, UK). Backscatter detection ( $173^\circ$  angle) was employed. Stock solutions (1 mg/mL for the size distribution measurements and 1.5 mg/mL for the molecular weight measurements) of each polymer were prepared by stirring purified (previously precipitated) samples in filtered ( $0.45 \mu\text{m}$ ) 0.05 M NaCl aqueous solution for at least 6 h. The stock solutions were left to rest overnight prior to use. In chain size measurements, the respective stock solutions were diluted up to a point that ensured an adequate attenuation level, avoiding multiple scattering (approximately in the ratio 1:7). Dilution series of 5 solutions in the concentration range 0.1–1.5 mg/

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