



Facile synthesis of a new fluorogenic metal scavenging interpolymeric diamide based on cellulose and alginic acids



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ABSTRACT

A microwave assisted synthesis of a water soluble fluorogenic interpolymeric diamide has been described involving alginic acid and polyglucuronic acid (PGA) amide of ethylenediamine (EDA), through a monoamide of PGA and EDA, in good yields (>80 wt % in each step). PGA was prepared by TEMPO (2,2,6,6-tetramethyl piperidine-1-oxyl radical) mediated oxidation of cellulose of the halophytic plant *Salicornia brachiata*. The amides were characterized by spectral analyses. The fluorescence emission of the PGA amide was 7-fold greater than that of the interpolymeric diamide. PGA monoamide exhibited superior heavy metal ions [Pb(II) and Hg(II)] uptake properties to the diamide, the former showing optimum adsorptions of ions 398.8 and 282.8 mg/g, respectively. These materials may be of utility as potential sensors harnessing their fluorogenic and metal scavenging properties.

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1. Introduction

Interpolymer complexes are formed by coupling of various macromolecules. They have been known for a considerable period of time with biocompatibility, adhesive, gelling, and specific drug delivery applications.^{1–3} Cellulose and alginic acid are renewable natural resources; most of their derivatives are biodegradable and functional. Cellulose derivative based interpolymeric complex with alginate,⁴ chitin,⁵ chitosan,⁶ and gelatin⁷ have been studied and reported to be useful as ion exchange, metal absorbent, and as scaffold for tissue regeneration. Alginic acid based interpolymeric derivatives with chitin,⁸ chitosan,⁹ and gelatin^{10,11} also exhibited applications as delivery medium for protein drugs, hydrogel nerves conduit, and wound healing materials. Fluorescent polymeric derivatives have received growing attention due to their potential applications in sensory materials, screening assays for enzymes, detection of peroxides, plastic colorants, and electroluminescence devices.^{12–17} Various methods have been reported for the removal of heavy metals such as precipitation, chemical modification, filtration, and ion exchange are often ineffective or expensive, especially in removing heavy metal ions present in low concentrations. The removal of heavy metal ions by adsorption using modified biopolymer has been widely studied in the last decades due to its potential application in waste water treatment. Biopolymer containing reac-

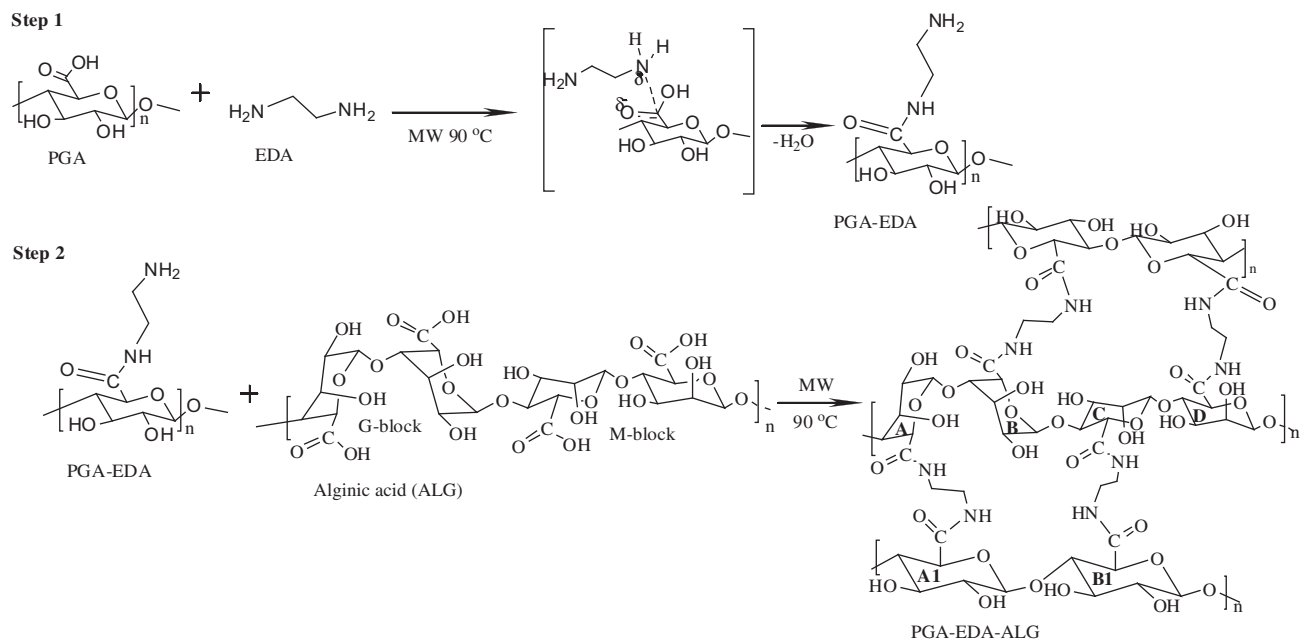
tive amine group can selectively bind heavy metal ions due to their high affinity to the amine group in comparison to the other functional groups.¹⁸ Hence, many attempts have been made to modify the biopolymer to introduce an amino group, subsequently imparting metal ion scavenging properties.^{19,20} Interpolymeric and/or fluorescent biopolymeric materials have also been reported in the literature to exhibit metal ion scavenging properties.^{21–23} We report herein for the first time to our knowledge, a facile synthesis of a new water soluble ethylenediamine cross linked fluorogenic interpolymeric diamide, based on the natural polymers glucuronic acid derived from cellulose and alginic acid (block co-polymer of mannuronic (M) and guluronic (G) acids; [Scheme 1](#)) in a continued effort of generating biopolymer based new materials in our laboratory.^{23–26} Heavy metal ion scavenging properties of these materials have been evaluated.

2. Results and discussion

The formation of the interpolymeric diamide happened in three functionalization steps ([Scheme 1](#)). The first step was the oxidation of cellulose to form polyglucuronic acid (PGA) ([ESI; Fig. S1](#)), forming thereby a reactive cellulose derivative, which in the next step was converted into a water soluble cross linkable glucuronamide (PGA-EDA) under microwave (MW) irradiation with EDA (1:1.3 mol equiv). The mono-amide derivative containing free amine groups (on the ethylenediamine residues) was then coupled with alginic acid (1:1 mol equiv.) under MW to form a water

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Scheme 1. (Step 1) Amidation reaction of PGA with EDA and (Step 2) amidation reaction of PGA-EDA with ALG.

soluble interpolymeric diamide (PGA-EDA-ALG). The mono-amide and the diamide derivatives were intensely fluorogenic, whereas both the parent polysaccharides alginic and glucuronic acids were not fluorescent and neither was EDA.

2.1. Mechanism of the reactions

The reaction mechanism for the TEMPO mediated oxidation (Fig. S1) followed by amidation (Scheme 1, step 1) has been reported in the literature.^{27–29} Apparently, a similar reaction mechanism was operating in the subsequent steps, where the carbonyl group of ALG got coupled with the free amine group of the ethylenediamine moiety present in the PGA-EDA derivative under MW irradiation, resulting in the interpolymeric diamide (PGA-EDA-ALG) (Scheme 1, step 2). Steric energy calculations (MM2) using ChemBio Draw 11.0 indicated that probably the interpolymeric diamide structure having amide cross linking involving ring connectivities A-A1 and C-B1 (Scheme 1) would be the most preferred one. This structure further indicated that the material would be porous, which was validated by its SEM image (vide infra Section 2.8). This structural feature has a similarity with the *o*-tolidine/alginic acid conjugate reported in the literature.²⁴

2.2. Yield and physicochemical property

Optimization studies revealed that microwave irradiation for 10 min at 90 °C led to the formation of the amide (PGA-EDA) and the diamide (PGA-EDA-ALG), in separate experiments, in good

yields, and purity. The yields of PGA, PGA-EDA, and PGA-EDA-ALG were 93.0%, 91.0%, and 82.6% having nitrogen contents 0%, 11.10%, and 6.30%, respectively (Table 1). The nitrogen content values indicated optimum stoichiometric efficiency of the diamidation reaction in presence of 1:1 (PGA-EDA/ALG). The degree of oxidation in PGA was 0.84, which was determined by the assay of carboxylic groups. The degree of substitution (DS) in PGA-EDA was 0.75, whereas it was 0.53 in PGA-EDA-ALG, obtained by Kjeldahl estimation of nitrogen contents. All these values were normalized with respect to the starting material. PGA-EDA and PGA-EDA-ALG contained 6.48% and 0.5% free amine groups (TNBS method)³⁰ and 9.1% and 37.5% free carboxylic groups, respectively, on the basis of the products obtained under optimized conditions. The free amino groups of PGA-EDA-ALG would result from the one free amino group of the ethylenediamine of PGA-EDA, which did not take part in the amidation reaction with the -COOH groups of ALG (Scheme 1, step 2). The free amine present in PGA-EDA-ALG was estimated to be 0.5% (Table 1). This was further corroborated by the reaction of the diamide with the natural cross linker genipin affording a light blue colored complex over 48 h.²⁶ The average molecular mass (M_z), number average molecular mass (M_n) and polydispersity index (PDI) of PGA, PGA-EDA, and PGA-EDA-ALG are given in Table 1. The results indicated that the polymer was not degraded during the reaction under microwave irradiation. No clear trend could be identified though in the molecular weight data, besides a steady increase in the PDI values $PGA < PGA-EDA < PGA-EDA-ALG$, as one would expect reflecting possible branching of the polymer molecules.

Table 1
Yields and physicochemical properties

Product	Yield (%)	N (%)	-NH ₂ (%)	-COOH (%)	DS	M_z	M_n	PDI ^c
PGA	93.0	NA ^a	NA ^a	20.3 ± 0.16	0.86	28271	4867	2.27
PGA-EDA	91.0	11.19 ± 0.13	6.48 ± 0.09	9.1 ± 0.10	0.75 ^b	27015	5200	2.55
PGA-EDA-ALG	82.6	6.30 ± 0.11	0.5 ± 0.04	37.5 ± 0.15	0.53 ^b	29952	4659	2.70

^a NA = Not applicable.

^b Values were deduced with respect to the DS value of PGA.

^c PDI = Polydispersity index.

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