



Synthesis and characterization of alginic acid ester derivatives



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ABSTRACT

Esters derivatives of alginic acid (Alg) were prepared in carboxylic acid/carboxylic acid anhydrides system by using aqueous perchloric acid as the catalyst. Degree of substitution of hydroxyl group of Alg was estimated to be 2, showing that the hydroxyl group of Alg was fully esterified. Alg acid esters showed the solubility to common organic solvents such as acetone and chloroform. In particular, alginic acid hexanoate formed self-standing solvent-cast film, although the film showed brittle mechanical behavior. Furthermore, Alg esters showed glass transition temperature (T_g) in a temperature range between 100 and 200 °C, that is in the same range as the conventional synthetic amorphous polymers. It was also shown that the T_g gradually lowered with the increasing acyl side chain length. These results show that Alg esters are plastic materials with tunable organosolubility and thermal properties.

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1. Introduction

Alginic acid (Alg) is a natural polysaccharide obtained from brown algae (Andriamanantoanina & Rinaudo, 2010a,b; Beale & Foster, 1996). Alg consists of 1 → 4-linked β-D-mannuronic acid (M) and its C5 epimer, α-L-guluronic acid (G). Alg is an acidic polysaccharide bearing carboxyl group linked to C5 carbon (Gacesa, 1988). Therefore, Alg shows high hydrophilicity, pH-dependent viscoelasticity, and capability of gelation by multivalent metal cations (Andriamanantoanina & Rinaudo, 2010a,b; Grant, Morris, Rees, Smith, & Thom, 1973; Matsumoto & Mashiko, 1990). Furthermore, Alg has physiological functions such as biocompatibility and biodegradability (Gacesa, 1992; Vos, Haan, & Schilfgaard, 1997; Zhang et al., 2004). By utilizing these properties, films, gels, or particles of Alg have been developed for the medical and food applications (Andriamanantoanina & Rinaudo, 2010a,b; Gacesa, 1992; Grant et al., 1973; Matsumoto & Mashiko, 1990; Otterlei et al., 1991; Tavassoli-Kafrani et al., 2016; Vos et al., 1997; Zhang et al., 2004). On the other hand, no examples for the development of thermoplastic and/or organo-soluble materials from Alg have been reported yet.

The lack of thermoplasticity and organosolubility of Alg is ascribed to the existence of carboxyl and hydroxyl groups, both contributing to formation of intra- and inter-molecular hydro-

gen bonds (Braccini, Grasso, & Pérez, 1999). On the other hand, these functional groups can be utilized as reaction points for the chemical modification (Pawar & Edgar, 2012; Ynag, Xie, & He, 2011). From this viewpoint, various types of functional side groups have been introduced by esterification or etherification with hydroxyl group or by amidation with carboxyl group (Pawar & Edgar, 2011; Schweiger, 1962a; Schweiger, 1962b; Siddhanta, Sanandiya, Chejara, & Kondaveeti, 2015; Skjåk-Bræk, 1989). However, thermoplastic materials from covalently modified Alg still have not been developed yet.

In this paper, we report the first development of thermoplastic and organosoluble materials from Alg by esterification with carboxylic acids having different acyl chain lengths. We also report that the properties of the ester derivatives of Alg are varied by the chain length of carboxylic acid.

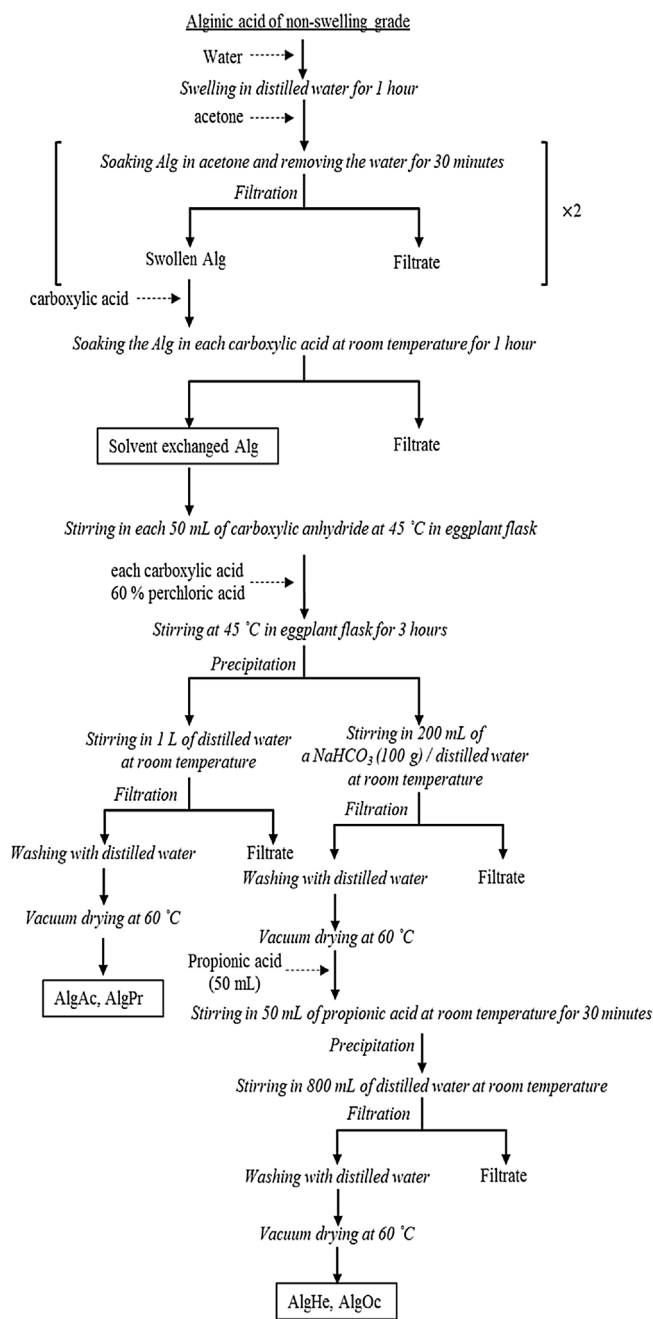
2. Materials and methods

2.1. Materials

Alginic acid (Alg) (M/G = 48/52) was purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. Carboxylic acids (acetic, propionic, hexanoic, and octanoic acid) and their anhydrides except octanoic anhydride were also purchased from Wako Pure Chemical Industries. *n*-Octanoic anhydride was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. All other reagents were commercially obtained and used without further purification.

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Scheme 1. Procedures for pretreatment and esterification of alginic acid.

2.2. Pretreatment and esterification of Alg by solvent exchange

Scheme 1 shows the whole process of pretreatment and esterification of Alg. In order to allow easy access of the esterification reagents to the Alg molecules to achieve efficient esterification, Alg was pretreated by the following procedures; Firstly, Alg was swollen in 200 mL of distilled water for 1 h. After removing the distilled water by stirring with acetone, acetone-exchanged Alg was stirred in the 100 mL of carboxylic acid and then filtered.

After the pretreatment, Alg was stirred in carboxylic acid anhydride (50 mL) at 45 °C. Mixture of carboxylic acid (50 mL) and 60% aqueous perchloric acid (0.5 mL) as the esterification catalyst was added to the mixture of carboxylic anhydride and Alg. And the reaction mixture was then stirred at 45 °C for 3 h and poured into 1 L of distilled water. The precipitate was recovered by filtration using No. 5A filter paper, washed with distilled water for several times,

and dried *in vacuo* over night to give 2.0 g of alginic acid acetate (AlgAc) or 7.2 g of propionate (AlgPr).

In the case of preparation of Alg hexanoate (AlgHe) and Alg octanoate (AlgOc) esters, the reaction mixture was poured into a sodium bicarbonate (100 g)/water (200 mL) solution. The precipitate was recovered by filtration, washed with distilled water, and dried *in vacuo* to obtain sodium salts of AlgHe and AlgOc. These sodium salts were transformed to carboxylic acid form by dissolving in propionic acid (50 mL), and precipitated in distilled water (800 mL). The precipitates were recovered by filtration, washed with distilled water, and dried *in vacuo* to obtain AlgHe (6.2 g) and AlgOc (11.1 g).

2.3. ¹H NMR measurement

500-MHz ¹H NMR spectra of Alg esters were obtained by using JNM-ECA500 FT-NMR (JEOL Resonance, Tokyo, Japan) spectrometer at 25 °C. Samples for NMR analyses were prepared by dissolving 10 mg of the Alg esters in 0.75 mL of trifluoroacetic acid-*d* (TFA-*d*) (99.5% atom D, Sigma-Aldrich, Co. Ltd., St. Louis, MO, USA).

¹H NMR (δ (ppm), in trifluoroacetic acid-*d*): AlgAc (2.2 (–OOCCH₃)), AlgPr (1.22 (–OOCCH₂CH₃), 2.5 (–OOCCH₂CH₃)), AlgHe (0.9 (–OOC(CH₂)₄CH₃), 1.3 (–OOC(CH₂)₂(CH₂)₂CH₃), 1.6, 1.7 (–OOCCH₂CH₂(CH₂)₂CH₃), 2.5 (–OOCCH₂(CH₂)₃CH₃)), AlgOc (0.8 (–OOC(CH₂)₆CH₃), 1.3 (–OOC(CH₂)₂(CH₂)₄CH₃), 1.6, 1.6 (–OOCCH₂CH₂(CH₂)₄CH₃), 2.4, 2.4 (–OOCCH₂(CH₂)₅CH₃)).

Degree of substitution (DS) of Alg esters were calculated from the spectra by

$$DS = \frac{I_{\text{CH}_3}}{\frac{I_{\text{Ring-H}}}{5}} \quad (1)$$

where I_{CH_3} and $I_{\text{Ring-H}}$ denote the peak area of the methyl proton (CH₃) the ring proton, respectively.

2.4. Gel permeation chromatography (GPC)

Number and weight-averaged molecular weights (M_n and M_w) and polydispersity value (M_w/M_n) of Alg and its ester derivatives were estimated by gel permeation chromatography (GPC) at 40 °C. Alg was transformed to sodium form and dissolved in 0.2 M aqueous sodium chloride. The Alg solution was eluted at 1 mL/min and permeated through linearly connected polystyrene columns (SB-806 and SB-804, 7.8 mm i.d. \times 300 mm for each column, Shodex Co. Ltd., Tokyo, Japan). Alg esters, dissolved in *N,N*-dimethylacetamide (DMAc) with the concentration of 3 mg/mL, were eluted at 0.8 mL/min and permeated through polystyrene column (KD-804, 7.8 mm i.d. \times 300 mm, Shodex Co. Ltd.). Calibration curves for each condition were obtained by using pullulan standards (Shodex Co. Ltd.). As shown later, number-average degree of polymerization (DP_n) was estimated from the M_n by taking DS into account.

2.5. Solubility test and preparation of solvent-cast films

Solubility of Alg and its derivatives were investigated by dispersing 5 mg of Alg or each derivatives in 2 mL of water or the following organic solvents at the room temperature: methanol, acetone, chloroform, DMAc, dimethylsulfoxide (DMSO), and TFA.

AlgPr, AlgHe, AlgOc (250 mg each) were dissolved in acetone (10 mL) and casted on Teflon[®] petri dish (5 cm diameter). The solvent was slowly evaporated at room temperature.

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