

Alginate Polyelectrolyte Ionotropic Gels. VI. Novel Synthesis of Diketoalginates as Biopolymer Precursors

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SYNOPSIS

Sodium 2,3-diketoalginate was quantitatively prepared by the oxidation of sodium alginate with potassium permanganate in alkaline solution at pH's > 12. The yield was 96.5%. The structure of the diketone was elucidated by microanalysis and spectroscopic data. It was found that the diketoalginate caused no gelation or precipitation with copper (II), nickel (II), or cobalt (II) divalent metal ions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Alginic acid is a polyelectrolyte that consists of D-mannuronic and L-guluronic acid units linked through $\beta(1-4)$ positions.¹⁻⁴ It is well known that solutions of alkali salts of some anionic polyelectrolytes containing carboxylate groups such as alginates are transformed to metal alginate ionotropic gels through the diffusion of polyvalent metal ion electrolytes in their sols. This sol-gel transformation was explained by assuming cross-linkage through the polyvalent metal ion involving carboxylate and hydroxyl groups of the macromolecular chains forming a large molecule.⁵

Many publications have been reported on methylation, hydrolysis, esterification, and degradation of alginates.⁶⁻¹⁰ However, the oxidation of such a natural polymer has received little attention.¹¹ In view of the foregoing ideas, in addition to our interest in the oxidation of dihydric alcohols,¹² synthetic,¹³ and natural polymers,¹⁴ the oxidation of alginate by alkaline permanganate is of great interest to present a facile synthesis of diketoalginate to be used as a precursor for the synthesis of new biopolymers.

EXPERIMENTAL

Sodium alginate (BDH grade) with molecular weight 75,000 was used without further purification.

All other materials were of analytical grade. Twice-distilled water was used in all preparations. Infrared spectra were recorded on a Pye-Unicam SP 200-G spectrophotometer, using the KBr pellet technique. The intrinsic viscosity of diketoalginate (0.5% w/v) in H₂O was determined at 30°C using an Ubbelohde suspended level visometer. Elemental analyses were carried out with a Perkin-Elmer 240 C microanalyzer.

Preparation of Diketoalginate

Sodium alginate powder (5 g) was dissolved in 400 mL of deionized water whose pH was previously adjusted to pH \geq 12 using sodium hydroxide. This process was performed by stepwise addition of the powder alginate while rapidly stirring the solution to avoid formation of a lumpy precipitate that swells with difficulty. To this solution, 7.96 g of potassium permanganate was added portionwise, then 8.3 g of sodium fluoride was added to this mixture while stirring. The reaction mixture was stirred for 24 h at room temperature, the formed MnF₄ was filtered off, and the solution was concentrated to 50 mL using a rotary evaporator. A portion of this concentrated solution was acidified using dilute acetic acid and the formed diketoalginic acid was precipitated by ethanol. The solid product was filtered off, washed several times with ethanol, dried under vacuum, and then subjected to elemental analysis and IR spectroscopy.

ANAL: Diketoalginate C₆H₄O₆ (172): Calcd (found): C, 41.86 (41.56); H, 2.35 (2.29). IR: 3450

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(OH of COOH group); 1750–1730 (broad) (C=O of α -diketone); 1700–1670 (C=O of COOH group); and 1270 cm^{-1} (C—O—C of alginate).¹⁵

2,4-Dinitrophenyl Hydrazone Derivative

ANAL: $\text{C}_{18}\text{H}_{12}\text{O}_{12}\text{N}_8$ (532): Calcd (found): C, 40.60 (40.58); H, 2.25 (2.28); N, 21.05 (21.01). IR: 3430 (OH of COOH group); 3310 (NH of hydrazone); 1680 (C=N of hydrazone); 1230 cm^{-1} (C—O—C of alginate).

Dioxime Derivative

ANAL: $\text{C}_6\text{H}_6\text{O}_6\text{N}_2$ (202): Calcd (found): C, 35.64 (35.61); H, 2.97 (2.98); N, 13.86 (13.72). IR: 3330–3355 (OH of COOH and oxime); 1670 (C=N); 1680 (C=O of COOH) 1230 cm^{-1} (C—O—C of alginate).

Chelation with Polyvalent Metal Ions

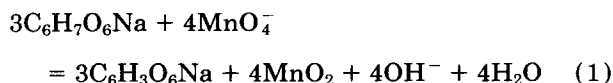
Mixing of 0.02 mol diketoalginate dissolved in 25 mL water with 0.02 mol of the corresponding metal chloride Cu(II), Ni(II), and Co(II) ions dissolved in 10 mL water, followed by heating for 15 min, failed to gelatinize or precipitate with these divalent metal ions. Hence, no chelation occurred.

Polymerization Test

The possibility of formation of free radicals was examined by adding a few drops of acrylonitrile to the reaction mixture. Under the experimental conditions of $[\text{MnO}_4^-] = 5 \times 10^{-2}$, $[\text{acrylonitrile}] = 0.005 \times 10^{-2}$, $[\text{alginate}] = 2.5 \times 10^{-2}$, $[\text{OH}^-] = 5 \times 10^{-2}$ mol dm^{-3} at 25°C, no polymerization was observed, indicating that the reaction did not proceed via a free-radical mechanism.

RESULTS AND DISCUSSION

Sodium alginate sols can be readily oxidized by the alkaline permanganate ion to give the corresponding ketoalginates. This depends on the stoichiometric molar ratio of the reactants and the reaction conditions. The stoichiometry of the overall reaction can be expressed by the equation



where $\text{C}_6\text{H}_7\text{O}_6\text{Na}$ denotes the alginate and $\text{C}_6\text{H}_3\text{O}_6\text{Na}$ is the diketoalginate.

It is well known that manganese (IV) tends to complex with the fluoride ion to form MnF_4 , which can be easily removed from the reaction mixture by filtration after the reaction is complete [or it can be reduced to Mn(II) salts by addition of NaHSO_3 or SO_2]. Therefore, to avoid the formation of colloidal MnO_2 , which filtered with difficulty, a stoichiometric amount of sodium fluoride is added to the redox reaction mixture.

The diketone structure was based on elemental analysis and infrared spectroscopy. The diketoalginate formed gave satisfactory elemental analysis and broad IR absorption bands at 1730–1730 cm^{-1} that characterize the carbonyl group of α -diketones,¹⁵ as shown in Figure 1. The disappearance of the absorption band of the OH group in the IR spectra indicates the complete oxidation of alginate to diketoalginate. This product was also reacted with 2,4-dinitrophenyl hydrazine and hydroxylamine to afford the corresponding bis-2,4-dinitrophenyl hydrazone and dioxime derivatives, which gave satisfactory elemental analysis and an IR absorption band at 1670 cm^{-1} (C=N). The yield was 96.5%.

The formed diketoalginate was easily soluble in water, but insoluble in most organic solvents such as acetone, acetonitrile, carbon tetrachloride, chlo-

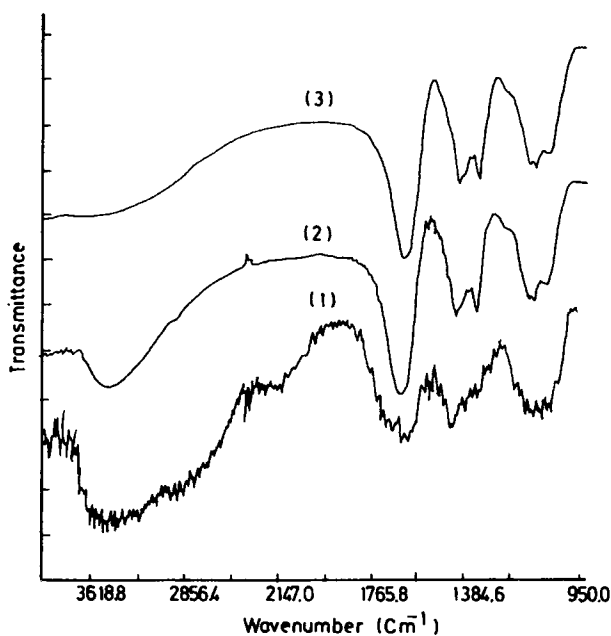
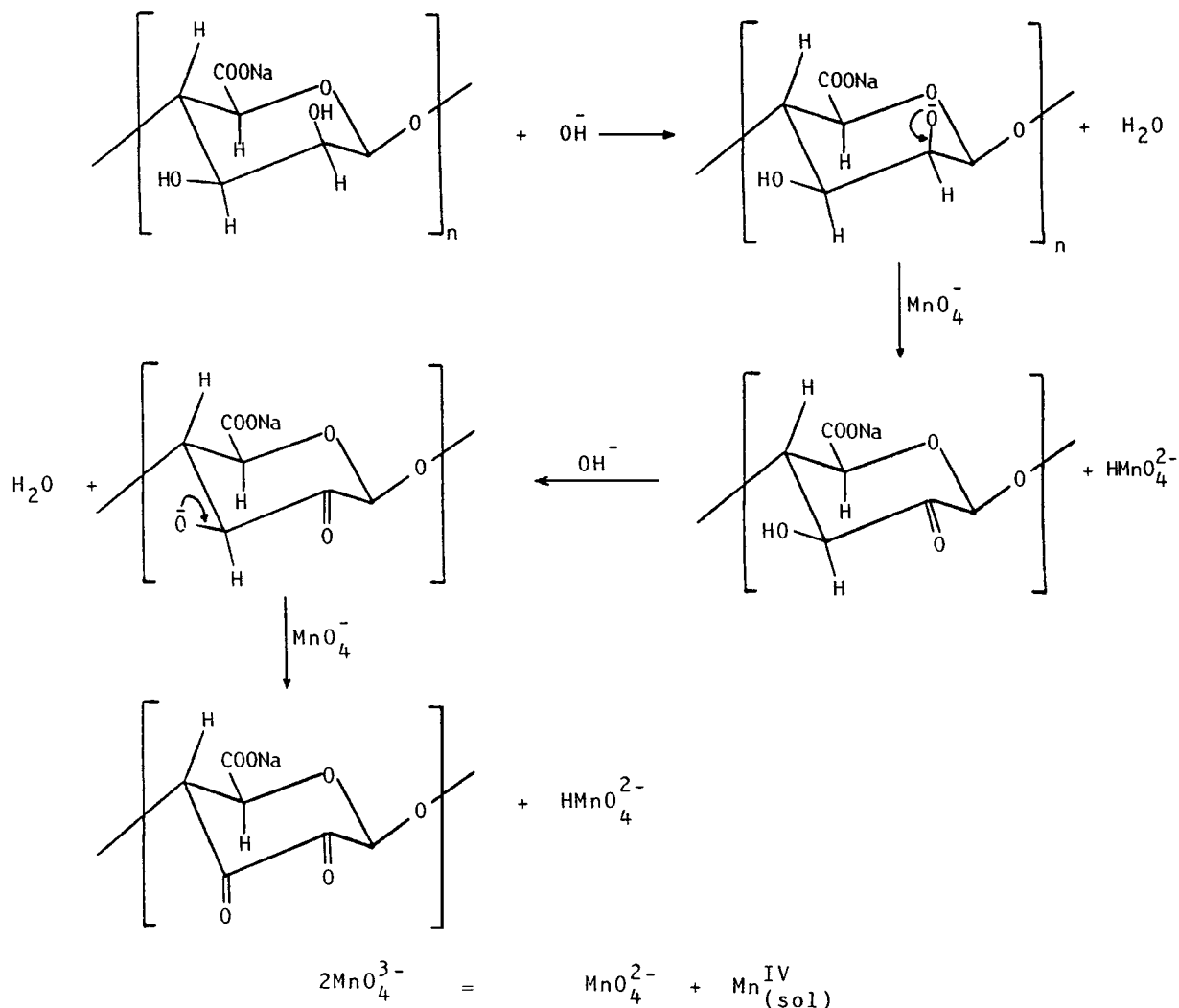


Figure 1 Infrared spectra of alginate and keto-derivatives: (1) alginate; (2) monoketoalginate; (3) diketoalginate.



Scheme I

reform, dichloromethane, and ethanol. The Mark-Houwink equation used to relate intrinsic viscosity was $[\eta] = KM^a$. For most high polymers, viscosity averages will be much closer to a weight-average than to a number-average molecular weight. The value of a for most polymers has been found to be around 0.7, where $a = 1$, $\bar{M}_v = \bar{M}_w$.¹⁶ The intrinsic viscosities of sodium alginate and diketoalginic were measured in the same solvent, which was water. Thus, by comparison of intrinsic viscosities of two similar polymers measured in the same solvent, sodium alginate, which is of known molecular weight (75,000), can be used to estimate the diketoalginic one.¹⁷

No gelation or precipitation was observed when the diketoalginic was added to most divalent metal ions such as Cu^{2+} , Ni^{2+} , and Co^{2+} metal ion elec-

trolytes. On the other hand, when the permanganate concentration is much smaller than the stoichiometric molar ratio, the reaction leads to the partial oxidation of alginates. The formed monoketoalginic does not change its affinity for chelation with most polyvalent metal ions. A detailed investigation of such monoketones is in progress in our laboratory.

The oxidation of alginate by alkaline permanganate was found to occur stepwise through an intermediate complex formation that was confirmed spectrophotometrically, as shown in Figure 2. A tentative reaction mechanism for the oxidation is shown in Scheme I.

The presence of 2,3-hydroxyl groups in the *cis* form may facilitate the attack of the MnO_4^- ion. The kinetics of oxidation of alginates by alkaline permanganate will be reported elsewhere.

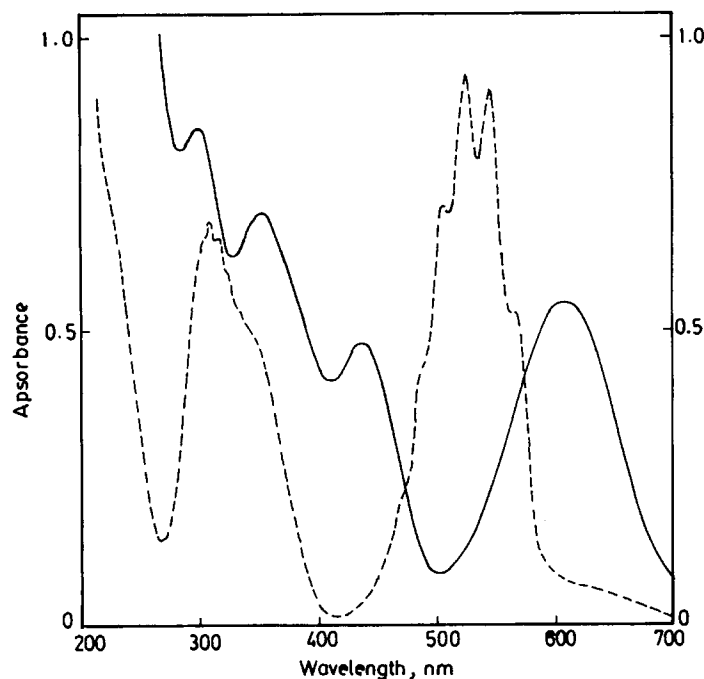


Figure 2 A spectral trace of the intermediates in the oxidation of alginate by the permanganate ion at $[\text{MnO}_4^-] = 4.29 \times 10^{-4}$, $[\text{alginate}] = 2.11 \times 10^{-4}$, $[\text{OH}^-] = 5 \times 10^{-2}$; (----) MnO_4^- ion; (—) intermediates.

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