

Novel Synthesis of Diketocarboxymethyl-Cellulose as Bipolymer Precursors

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ABSTRACT: 2,3-Diketocarboxymethylcellulose was prepared by the oxidation of carboxymethylcellulose (CMC) with potassium permanganate in alkaline solutions (pH ≥ 12) with a yield of 98.1%. IR spectroscopy and microanalysis have elucidated the chemical structure of the synthesized macromolecule (CMCK). A tentative reaction mechanism for oxidation is suggested. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1019–1023, 2002

Key words: carboxymethylcellulose; permanganate; oxidation; ketones; polysaccharides

INTRODUCTION

Although permanganate ion is a powerful oxidizing agent for most organic substrates,^{1–6} the oxidation of macromolecules by this oxidant has received little attention.

Indeed, Hassan et al. have investigated the kinetics of oxidation of alginate,^{7,8} pectin,^{9,10} chitin,^{11,12} and poly(vinyl alcohol)^{13,14} as natural and synthetic macromolecules by this oxidant. They reported that the oxidations proceed through two distinct stages, where an intermediate complex with manganate (VI) as transient species is formed in the first stage. The second stage is relatively slow and involved the decomposition of such an intermediate to give the corresponding ketoderivatives and soluble manganese (IV) as reaction products.

Therefore, the present work is of great importance to obtain some information on the chemistry of oxidation of macromolecules in alkaline media and to compare the data with that obtained previously.^{15,16}

EXPERIMENTAL

Carboxymethylcellulose (CMC) used in this work was of the microgranule type (Merck reagent), the capacity of which is 1 mequiv/g. This reagent was used without any further purification. All other materials used were of analytical grade. Double-distilled water was used in all preparations. Infrared spectra were recorded on a Pye-Unicam SP3 100 spectrophotometer by using a KBr disc technique (4000–200 cm^{-1}). Elemental analyses were carried out with a Perkin–Elmer 240 C microanalyzer.

Preparation of Diketocarboxymethylcellulose

A measure of 5.0 g of CMC powder was dissolved in 250 cm^3 of deionized water the pH of which was

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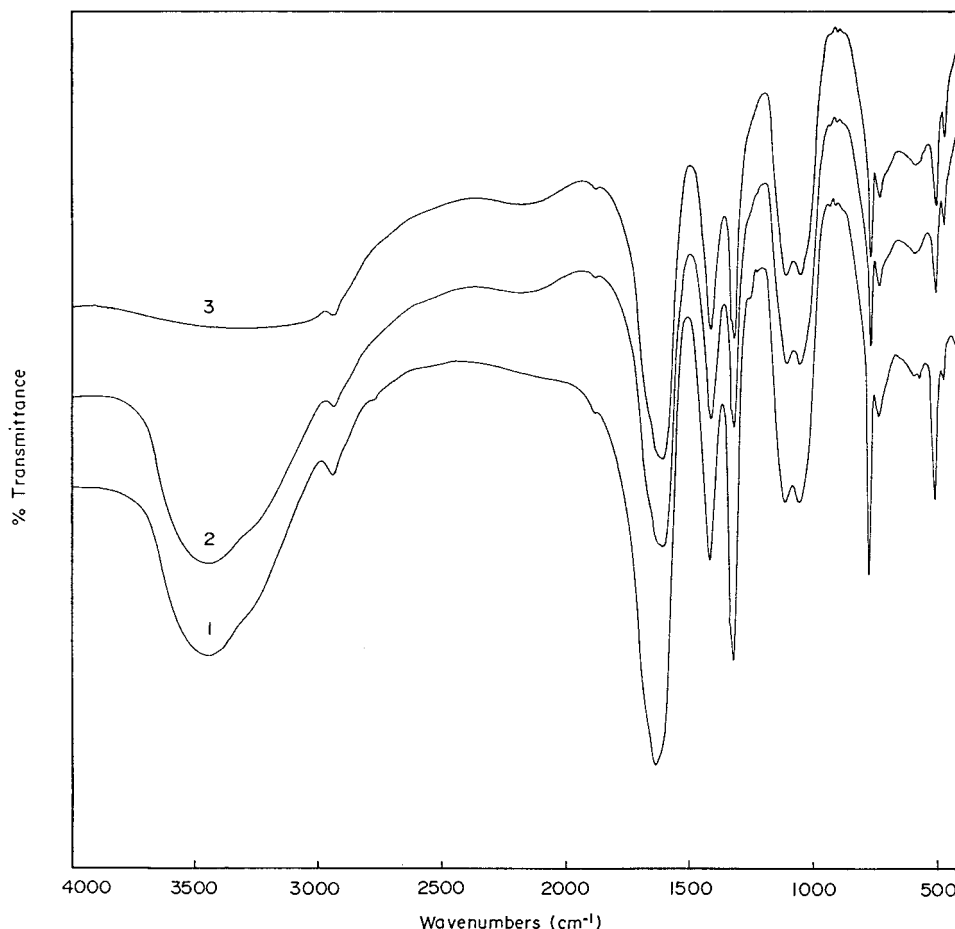


Figure 1 Infrared spectra of carboxymethylcellulose and its keto derivatives. 1, Carboxymethylcellulose; 2, monoketocarboxymethylcellulose; 3, diketocarboxymethylcellulose.

previously adjusted to $\text{pH} \geq 12$ by using sodium hydroxide. This process was performed by step-wise addition of the powder CMC while rapidly stirring the solution to avoid the formation of a lumpy precipitate that swells with difficulty. A 250 cm^3 solution containing 7.2 g potassium permanganate and 7.4 g sodium fluoride was added portion-wise to the CMC solution while stirring. The reaction mixture was stirred for about 48 h at room temperature. After this time, the MnF_4 formed was filtered off and the filtrate was concentrated to one-fifth of the original volume by using a rotary evaporator. A portion of this concentrated solution was acidified with acetic acid to a pH of $\sim 5-6$ and the formed diketocarboxymethylcellulose was precipitated with ethanol, dried under vacuum, and then subjected to elemental analysis and IR spectroscopy.

ANAL.: diketocarboxymethyl cellulose $\text{C}_8\text{H}_8\text{O}_7$ (216); Calcd (found): C, 44.44 (44.19); H, 3.70 (3.51). IR: 3447

(OH of COOH group), 1760–1730 (broad) ($\text{C}=\text{O}$ of diketone); 1690–1632 ($\text{C}=\text{O}$ of COOH group); and 1255 cm^{-1} ($\text{C}-\text{O}-\text{C}$ of CMC).¹⁷

2,4-Dinitrophenyl Hydrazone Derivative

ANAL.: $\text{C}_{20}\text{H}_{16}\text{O}_{13}\text{N}_8$ (576); Calcd (found): C, 41.67 (41.45); H, 2.78 (2.88); N, 19.44 (19.32). IR: 3410 (OH of COOH group); 3325 (NH of hydrazone); 1665 ($\text{C}=\text{N}$ of hydrazone); 1265 cm^{-1} ($\text{C}-\text{O}-\text{C}$ of CMC).

Dioxime Derivative

ANAL.: $\text{C}_8\text{H}_{10}\text{O}_7\text{N}_2$ (246); Calcd (found): C, 39.02 (39.13); H, 4.07 (4.13); N, 11.38 (11.27). IR: 3330–3360 (OH of COOH and oxime); 1675 ($\text{C}=\text{N}$); 1690 ($\text{C}=\text{O}$ of COOH) 1240 cm^{-1} ($\text{C}-\text{O}-\text{C}$ of CMC).

Polymerization Test

The possibility of formation of free radicals was examined by adding a few drops of acrylonitrile to

Time interval=30 s

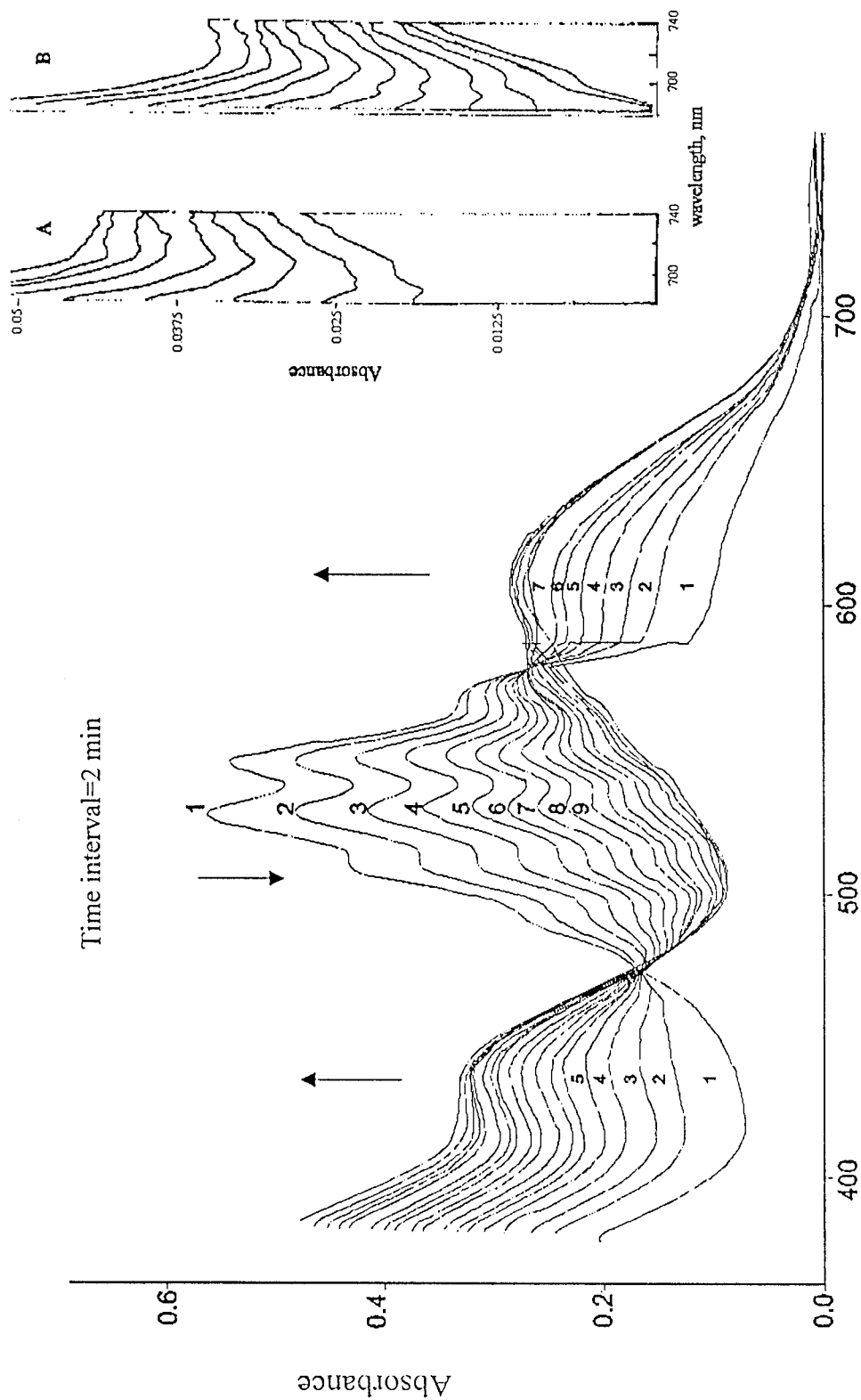
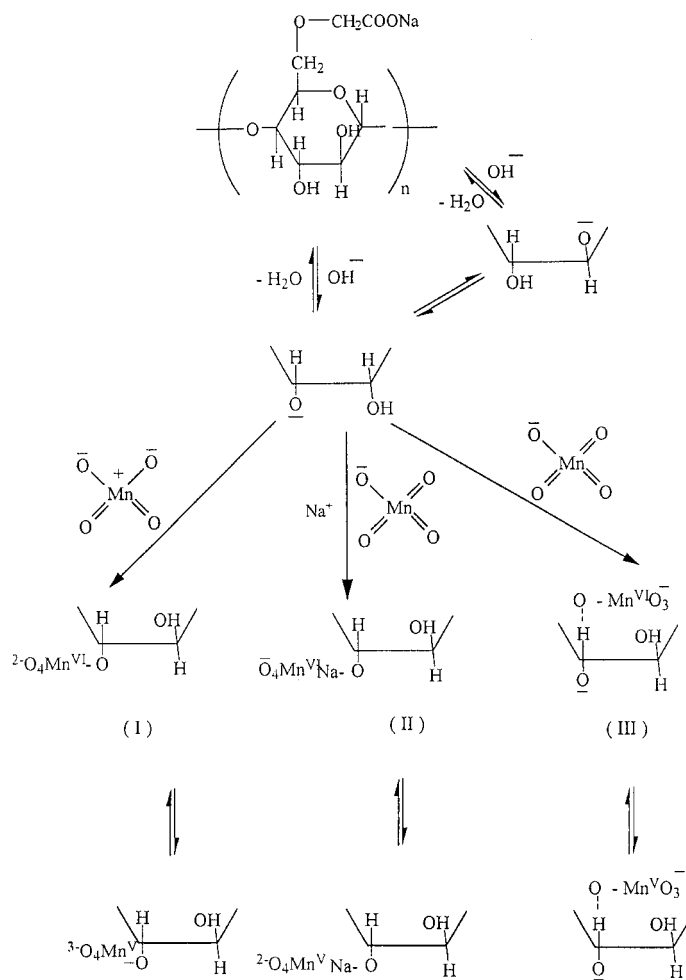
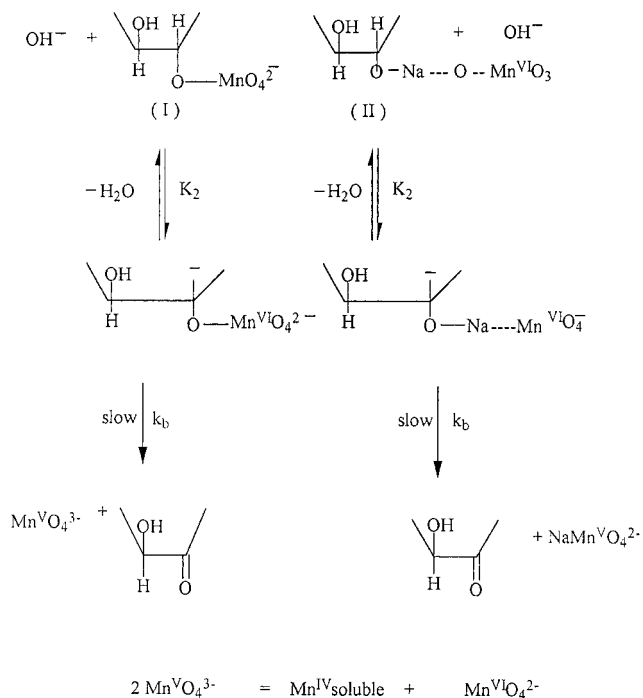


Figure 2 Spectral changes (300–700 nm) in the oxidation of carboxymethylcellulose by permanganate ion. $[\text{MnO}_4^-] = 2 \times 10^{-4}$; $[\text{CMC}] = 4 \times 10^{-3}$; $[\text{OH}^-] = 2 \times 10^{-2}$; $I = 0.1 \text{ mol dm}^{-3}$ at 20°C .

Formation



Decomposition

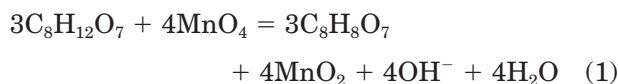


Scheme 1

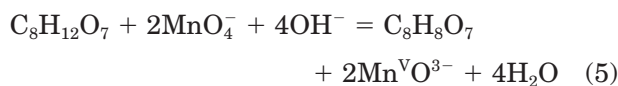
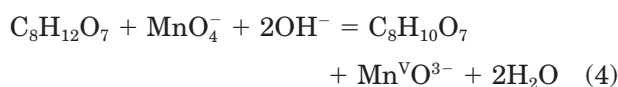
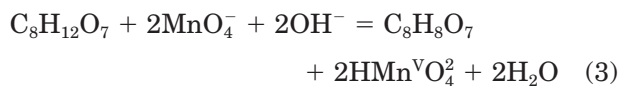
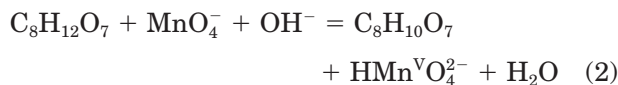
the reaction mixture. Under the experimental conditions of $[\text{MnO}_4^-] = 5 \times 10^{-2}$, $[\text{acrylonitrile}] = 0.005 \times 10^{-2}$, $[\text{CMC}] = 2.5 \times 10^{-2}$, $[\text{OH}^-] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ at 25°C , no polymerization was observed, indicating that the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

RESULTS AND DISCUSSION

The stoichiometry of oxidation of carboxymethylcellulose by potassium permanganate conforms to the following equation:



It was reported that the formation of mono- or diketoderivatives for the oxidation of polysaccharide^{7,8} by alkaline permanganate depends on the molar ratio of the reactants as well as the pH of the medium. Therefore, the influence of molar concentration of the oxidant and the pH of the medium on the oxidation product may be expressed as follows:



where $\text{C}_8\text{H}_{12}\text{O}_7$, $\text{C}_8\text{H}_{10}\text{O}_7$, and $\text{C}_8\text{H}_8\text{O}_7$ denote the carboxymethylcellulose, monoketo-, and diketocarboxymethylcellulose, respectively. Microanalysis and spectral data can identify these keto-derivatives.

Under our experimental conditions, the diketocarboxymethylcellulose is formed. This diketoderivative gave satisfactory elemental analysis and broad IR absorption bands at $1760\text{--}1730 \text{ cm}^{-1}$ (broad) that characterize the carbonyl group of α -diketones.¹⁷ The disappearance of the absorption band of the OH group in the IR OH

groups indicated the complete oxidation of both OH groups in CMC to the corresponding ketones. This product was also reacted with 2,4-dinitrophenyl hydrazine and hydroxylamine to afford the corresponding bis-2,4-dinitrophenyl hydrazone and dioxime derivatives, respectively, which gave satisfactory elemental analysis and spectroscopic data, as shown in Figure 1. The yield was 98.1%.

The oxidation of CMC was found to proceed stepwise through formation of detectable of an intermediate complex, $[\text{CMC}, \text{Mn}^{\text{VI}}\text{O}_4^{2-}]$, with manganate (VI) as the transient species that was confirmed spectrophotometrically (Fig. 2), followed by a slow decomposition of this intermediate to give the ketoderivative products.¹⁸ A tentative reaction mechanism for oxidation is illustrated in Scheme I.

Similar reaction mechanisms for oxidation of some macromolecules by this oxidant in alkaline solutions have been reported elsewhere.^{7,9,13,15,16}

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