

Synthesis of Dextran Dicarboxylic Acid and Investigation of Its Complexes with Metal Ions in Aqueous Solutions

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ABSTRACT: Dextran dicarboxylic acid was successfully synthesized by the direct oxidation of dextran with sodium chlorite and its characterization was realized by means of IR and NMR spectrometers. Viscometric measurements were done by metal-polymer complexes with Cu(II), Ni(II), and Cd(II) in aqueous solution at 25°C and Ni(II) was found to be the most effective ion in decreasing the viscosity of the

polymer solution than the other two metal ions, whereas Cd(II) was the least effective cation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2262–2265, 2004

Key words: functionalization of polymers; metal-polymer complexes; synthesis

INTRODUCTION

The complexation of low molecular weight compounds with various metal ions has received a great deal of attention.^{1,2} The characteristics of complex formation, such as stability constants, structure, and composition of complexes, are of interest to many investigators.

The polymer-metal complexes are very important in fields such as biocompatible polymers, liquid crystals, and superconducting materials and they have been shown to be useful materials for the removal of metal ions from diluted solutions.³ Transition metal ion pollutants in aqueous systems can be removed by using various polymeric ligands with different functional groups.

Dextran has oxygen atoms found at three different positions. Two of them are placed at the backbone as a bridge oxygen and as a ring oxygen, respectively. The third one is in the hydroxyl group of the side chain, which can be functionalized by the oxidation of dextran, as shown below:

Dextran dialdehyde and dextran dicarboxylic acid were synthesized by the oxidation of dextran by using different oxidizing agents in the literature.⁴ This study deals with the synthesis and characterization of dextran dicarboxylic acid by the reactions of dextran with sodium chlorite. The present study also describes the viscometric measurements done by the metal-polymer complexes with Cu(II), Ni(II), and Cd(II) in aqueous solution at 25°C.

EXPERIMENTAL

Materials

In this study, commercial dextran with a molecular weight of 70,000 g mol⁻¹ (T 70, $M_n = 46,800$ g mol⁻¹) from Pharmacia Fine Chemicals AB (Uppsala, Sweden) was used as the polymer sample. Ethylene glycol (Analar), sodium chlorite (Analar Poole, United Kingdom), hydrochloric acid (BDH Poole, United Kingdom), CuCl₂·2H₂O (BDH), CdCl₂·2H₂O (BDH), and NiCl₂·6H₂O (BDH) were all commercial compounds and were used without further purification. The polymer sample was dried and stored in a desiccator over MgSO₄. Polymer solutions were freshly prepared before use.

Polymer synthesis

Dextran dicarboxylic acid was synthesized similar to the method of synthesis of dextran dialdehyde by using sodium chlorite instead of sodium metaperiodate.⁵ Dextran was treated with sodium chlorite (10 molecules per one hydroxyl group of dextran) at room temperature where pH = 3, so that hydroxyl groups were 80% oxidized to carboxyl groups. The conversion was determined by means of reduction of the OH band in the IR spectrum.

The reaction was carried out in a glass-stoppered flask in the dark. The solution was dialyzed against running water for 48 h and then against acetate buffer at pH = 3 for 8 h. Acetate ions were removed by dialyzing the solution against water for 4 h. The resulting solution was then lyophilized.

The sodium salt of dicarboxy dextran formed in such a reaction was easily soluble in water. Dicarboxy

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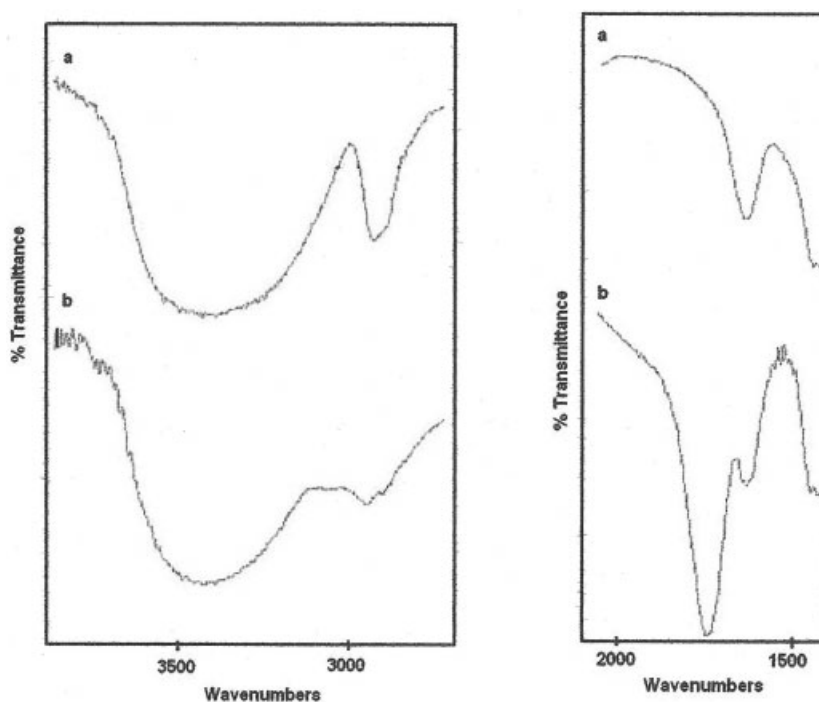


Figure 1 FTIR absorbance spectra of (a) dextran and (b) dextran dicarboxylic acid.

dextran was obtained in the form of an acid by treating the sodium salt with hydrochloric acid and was characterized by IR and NMR spectrometers. IR spectrum was obtained on a Mattson 1000 FTIR spectrometer at room temperature; absorption maxima are reported in wave numbers (cm^{-1}). NMR spectrum was recorded on a Bruker AC-200 (200 MHz) NMR spectrometer; CDCl_3 was the solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts are reported in ppm (δ) downfield from the signal of TMS.

The viscometric behavior of dextran dicarboxylic acid/water and dextran dicarboxylic acid/ Cu^{2+} , dextran dicarboxylic acid/ Ni^{2+} , and dextran dicarboxylic acid/ Cd^{2+} solutions were performed at 25°C by using a Ubbelohde-type capillary viscometer. The temperature of the thermostat was controlled within the range of $\pm 0.1^\circ\text{C}$ and the flow times were measured with a digital accuracy of ± 0.1 s. The concentration of dextran dicarboxylic acid in solutions was changed in the range of 0.2–0.06 g/dL.

RESULTS AND DISCUSSION

Introduction of carboxyl groups into the macromolecule of dextran was realized by a stepwise mechanism (i.e., periodate oxidation of dextran has resulted in the production of a derivative of dextran containing aldehyde groups, dextran dialdehyde, and subsequent oxidation of dextran dialdehyde with sodium chlorite has permitted the introduction of carboxyl groups into

the structure).⁵ In this study, dextran dicarboxylic acid was directly synthesized by the reaction of dextran with sodium chlorite. Stepwise mechanism to convert dextran into dextran dialdehyde and then converting dextran dialdehyde to dextran dicarboxylic acid was not necessary because dextran was successfully converted to dextran dicarboxylic acid by means of sodium chlorite. When the IR spectra of dextran and dextran dicarboxylic acid were compared, a very broad characteristic band of $-\text{OH}$ group belonging to carboxylic acid moiety in the range of $2600\text{--}3600\text{ cm}^{-1}$ appeared in the spectrum of dextran dicarboxylic acid different from the spectrum of dextran itself. In the IR spectrum of dextran, a broad band of polymeric alcohols was placed in the range of $3200\text{--}3400\text{ cm}^{-1}$. Besides the above-mentioned broad band of carboxylic acids, a band at 2500 cm^{-1} appeared in the spectrum of dextran dicarboxylic acid arising from the dimeric property of acids. In addition, a sharp and intense $\text{C}=\text{O}$ band was observed at 1745 cm^{-1} . The intensity of the band at 1625 cm^{-1} belonging to overtone and combination bands of alcohols in the spectrum of dextran was highly reduced in the corresponding IR spectrum of dextran dicarboxylic acid (Fig. 1).

The $^1\text{H-NMR}$ results support the IR findings. Thus, the three different OH peaks belonging to dextran spectrum at $\delta = 3.75\text{ ppm}$, $\delta = 3.60\text{ ppm}$, and $\delta = 3.50\text{ ppm}$ of the dextran spectrum appeared at nearly the same chemical shift, respectively; in the corresponding $^1\text{H-NMR}$ spectrum of carboxylic acid derivative of dextran, however, they were reduced according to the

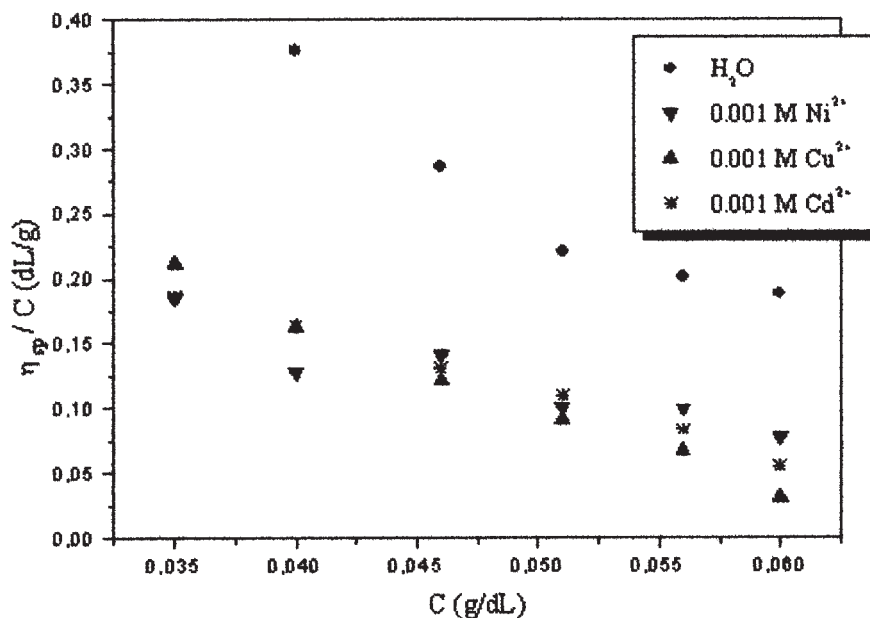


Figure 2 Intrinsic viscosities of dextran dicarboxylic acid in (a) 0.001M H₂O, (b) 0.001M Cu²⁺, (c) 0.001M Ni²⁺, (d) 0.001M Cd²⁺.

conversion of OH groups to carboxylic acid function. The formation of carboxylic acid moiety can also be proved by the appearance of acidic peak in the spectrum of carboxylic acid derivative of dextran at $\delta = 10$ ppm, which was not observed in dextran spectrum.

Viscometric measurements were carried out for dextran dicarboxylic acid and those of Me²⁺ complexes. In the concentration range studied, the reduced viscosity (η_{sp}/C_p) can be generally represented by the well-known relation,

$$\eta_{sp}/C_p = [\eta] + K_H[\eta]^2 C_p \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, K_H is the Huggings constant, and C_p is the polymer concentration.⁶ Intrinsic viscosity is a measure of hydrodynamic volume of polymer coil in solution and represents the polymer/solvent and polymer/solvent/additive interactions, depending on the nature and concentration of the cosolute in the studied systems. Extrapolation of the reduced viscosity to infinite dilution using this empirical dependence gives the intrinsic viscosity values of the expanded polymer coils.

The physicochemical properties of solutions of synthetic water-soluble metal polymers have gained attention mainly because of the hydrodynamic properties, among which the intrinsic viscosity is considered in great detail. Many water-soluble polymers were synthesized, such as anionic polyelectrolytes containing acrylic, methacrylic, and sulfonic acid groups, and their viscometric properties were studied.⁷⁻¹⁰ Practically all these water-soluble polymers exhibit typical

polyelectrolyte behavior (i.e., decrease in the reduced viscosity with an increase in polyelectrolyte concentration).

According to Figures 2 and 3, the water-soluble dextran dicarboxylic acid exhibits typical polyelectrolyte behavior; that is, reduced viscosity decreases with an increase in polyelectrolyte concentration. This behavior may be interpreted such that as the polyelectrolyte concentration decreases, the ionization degree increases and the produced ions form an ionic environment in a size that is larger than the diameter of polymer coil. The repulsion among the ions increases the rigidity of the chain, expanding the polymeric coil with a consequent increase of the viscosity.¹¹ Viscometric measurements may help in the understanding of the polymer-metal interaction phenomena in aqueous solution, including polymer-metal complex formation. The intrinsic viscosity values of water-soluble polymer-metal complexes may indicate the type of polymer-metal ion interaction. In this sense, for a better understanding of the phenomena, it is necessary to study the behavior in aqueous solution of polymers and polymer-metal complexed ions.¹² At a constant concentration of dextran dicarboxylic acid, an increase in the amount of Cu(II), Ni(II), and Cd(II) ions caused a decrease in the viscosity.¹³ Reduced viscosity of dextran dicarboxylic acid decreased with increasing metal ion concentration. The increasing metal ion concentration increases the ionic strength of the solution outside the polymer coil relative to that inside and also reduces the thickness of the layer of bound counterions around the chain. These effects cause the chain to contract.

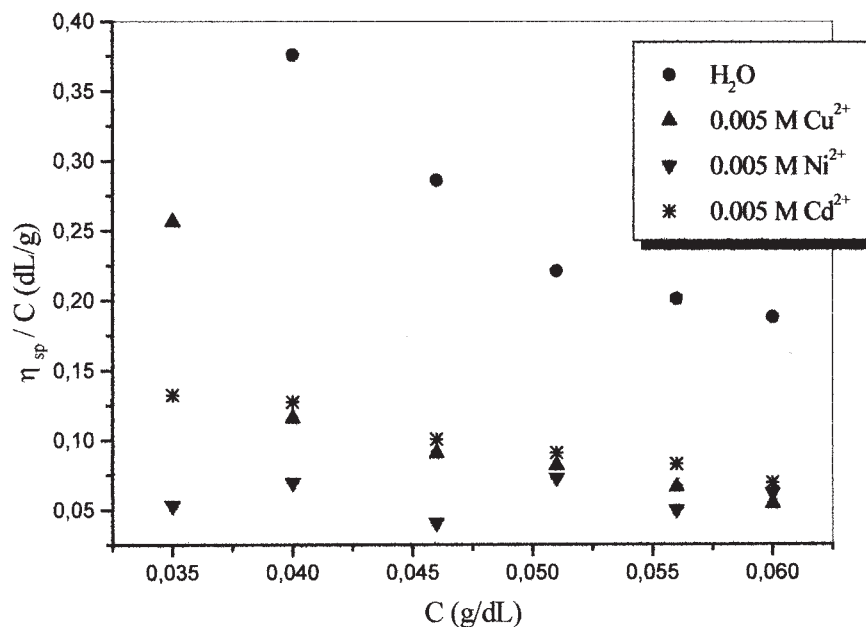


Figure 3 Intrinsic viscosities of dextran dicarboxylic acid in (a) 0.005M H₂O, (b) 0.005M Cu²⁺, (c) 0.005M Cd²⁺, (d) 0.005M Ni²⁺.

The effect of different metal ions and their concentrations on viscosity of polymer (η_{sp}/C_p) are shown in Figures 2 and 3. As can be seen, Ni²⁺ ion is more effective than the other two metal ions (Cu²⁺ and Cd²⁺) in decreasing the viscosity of the polymer solution, whereas Cd²⁺ is the least effective cation.

Pearson classified various ligands containing nitrogen and oxygen atoms as hard and soft acids and bases depending on the charge density and the resonance form.¹⁴ According to Pearson's classification, Cu²⁺ and Cd²⁺ are known as soft acids and Ni²⁺ is borderline. However, H⁺ is classified as a hard acid. From this approach, maximum interaction should be expected between dextran dicarboxylic acid and Ni²⁺, so that, from viscometric measurements, interaction with dextran dicarboxylic acid was found in the following order: Ni²⁺ > Cu²⁺ > Cd²⁺. The difference in the complexation of Cu²⁺ and Cd²⁺ ions with the polymer might be explained by the steric hindrance of Cd²⁺ to interact with the carboxylate groups on dextran dicarboxylic acid because of their large size and difficult accessibility.

CONCLUSION

In this study, the synthesis and characterization of dextran dicarboxylic acid by means of IR and NMR spectra were investigated. According to viscometric

measurements of the metal-polymer complexes with Cu(II), Ni(II), and Cd(II) ions, Ni(II) was the most effective cation to decrease the viscosity of the dextran dicarboxylic acid.

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