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AFM studies on gelation mechanism of xanthan gum hydrogels

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Abstract

The effect of annealing on xanthan gum molecules was investigated using atomic force microscopy (AFM). The values of height and width of xanthan gum molecules in AFM images are ca. 1 nm, which strongly indicates that xanthan gum molecules extended on the mica surface are in mono- or double layers. When xanthan gum aqueous solution was annealed, a network structure was observed. In contrast, a network structure was not observed for non-annealed solution. AFM images provide direct information concerning oscillational change of the network structure. It is concluded that xanthan gum molecular chains in aqueous solution aggregate and dissociate in an oscillational manner with increasing annealing time and that a homogeneous network structure was formed by annealing at 40 °C for 24 h.
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1. Introduction

Xanthan gum is an extracellular polysaccharide from *Xanthomonas campestris* (Jansson, Kenne, & Lindberg, 1975). The primary structure according to Morris's paper (1995) is shown in Fig. 1. The secondary structure of xanthan gum has been investigated by the use of X-ray diffraction studies of oriented fibre and molecular modelling method (Moorhouse, Walkinshaw, & Arnott, 1977; Okuyama et al., 1980).

It is known that xanthan gum does not readily form hydrogels by the usual gelation method (Fujiwara, Iwanami, Takahashi, Tanaka, Hatakeyama, & Hatakeyama, 2000; Quinn, Hatakeyama, Takahashi, & Hatakeyama, 1994; Yoshida, Takahashi, Hatakeyama, & Hatakeyama, 1998). However, it was found that xanthan gum forms hydrogels when aqueous solutions are annealed at a temperature higher than the characteristic temperature and subsequently cooled (annealing and subsequent cooling induced gelation) (Takahashi, Hatakeyama, & Hatakeyama, 1998). When xanthan gum aqueous solutions were annealed at 40 °C, gel–sol transition temperature (T_{g-s}) was clearly observed by falling ball method (FBM) rheological measurement (Yoshida et al., 1998). Similar results were obtained for hyaluronan aqueous solution (Fujiwara, Takahashi, Hatakeyama, & Hatakeyama, 2000). Furthermore, gelation of gellan gum, which is a representative gel forming polysaccharide electrolyte, is accelerated when the gellan aqueous solutions are annealed in the sol state (Quinn, Hatakeyama, Yoshida, & Hatakeyama, 1993).

The above phenomena are found to correlate with the structural change of water restrained by polysaccharide molecules. When xanthan gum aqueous solutions were measured by differential scanning calorimetry (DSC), it

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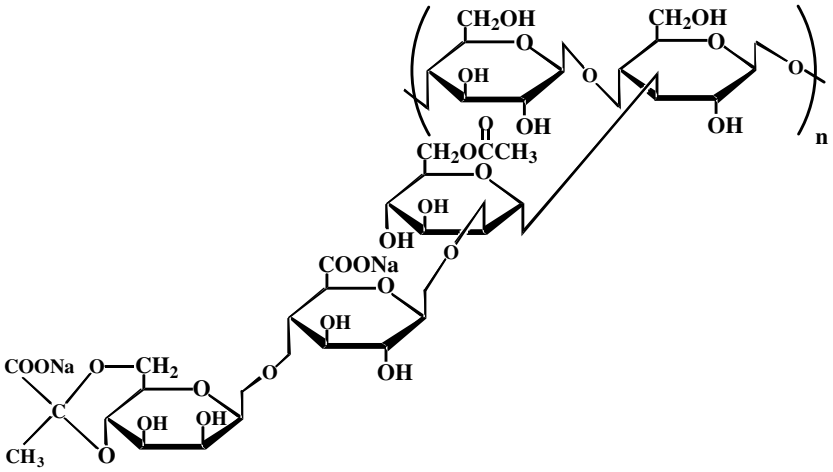

Fig. 1. Chemical structure of xanthan gum.

was found that the melting enthalpy (ΔH_m) of water changed oscillationally during the annealing process, and then approached a constant value (Takahashi, Hatakeyama, & Hatakeyama, 2000). In the initial stage of annealing, the assemblies of polysaccharide molecules dissociate by desorbing water molecules. Subsequently, the solution homogenizes by the diffusion of polysaccharide molecules, which are removed from the assemblies. After the homogenization of the system was attained, the xanthan gum molecules form a junction structure, which enables the system to form gels by adsorbing the non-freezing type bound water.

In this study, the effect of annealing on xanthan gum molecules is investigated using atomic force microscopy (AFM). By comparing morphological features and thermal data, the gelation process of xanthan gum hydrogels is clarified.

2. Experimental

2.1. Sample preparation

Xanthan gum in powder form was purchased from SIGMA, and xanthan gum was solved in pure water (Wako Chemical) and stirred at 25 °C. Xanthan gum aqueous solutions with concentration 10 or 20 g l^{-1} were prepared.

2.2. AFM measurement

Samples for AFM were prepared as follow. Ten grams per liter xanthan gum aqueous solution was annealed at 40 °C for 1 ~ 24 h (Fujiwara, Takahashi et al., 2000; Yoshida et al., 1998). One milliliter annealed or non-annealed 10 g l^{-1} (1%) xanthan gum aqueous solutions were diluted into 9 ml of pure water. This process was repeated. Ten nanograms per microliter (10×10^{-4}%) xanthan gum aqueous solutions were obtained. A drop of butanol was added to the xanthan gum diluted solutions. The 10 ng μl^{-1} xanthan gum aqueous solution was spread on freshly cleaved mica using a syringe. Samples spread on mica were dried in air overnight.

An SII Nano Technology Inc., atomic force microscopy (AFM) SPA300HV equipped with a controller (SPI3800N, SII Nano Technology Inc.) was used. Tapping mode in air was employed in the present study. The size of the geometrical shape of the needle and the sample widths were calibrated using the method reported previously (Hatakeyama & Hatakeyama, 2004).

2.3. DSC measurement

Aqueous solution of xanthan gum with concentration 20 g l^{-1} was used. An SII Nano Technology Inc., differential scanning calorimeter (DSC) EXSTAR 6000 equipped with a cooling apparatus was used. Temperature and enthalpy calibrations were calibrated using water. Dry nitrogen was used as a purge gas and the flow rate was 30 ml min^{-1}. The scanning rate was 10 °C min^{-1}. The sample mass was ca. 4 mg and an aluminum sealed-type sample-pan was used. The sample-pan was hermetically sealed and the total mass was recorded. A Sartorius ultramicro-balance ($\pm 0.1 \times 10^{-6}$ g) was used for sample mass measurements. The samples were annealed at 40 °C for 0 ~ 24 h in a DSC sample holder. The sample was cooled from 40 °C to −80 °C and heated from −80 °C to 80 °C. Liquid nitrogen was used a coolant.

3. Results

As described in the experimental section, 10 g l^{-1} xanthan gum aqueous solution was diluted 10 times and the dilution repeated three times. AFM observation was carried out at each stage of dilution. When concentration reached 10 ng μl^{-1}, clear micrographs showing xanthan gum molecules extended on the mica surface were obtained. On this account, all AFM measurements were carried out at concentration of 10 ng μl^{-1}.

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