

In situ observation of heat- and pressure-induced gelation of methylcellulose by fluorescence measurement



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ABSTRACT

In situ observation of heat- and pressure-induced gelation of methylcellulose (MC) aqueous solution has been studied by using dynamic viscoelastic and fluorescence measurements. The storage modulus G' decreased gradually first on heating, and then leveled off in the temperature range from 25 °C to 75 °C. Methylcellulose solutions were subjected to pressures up to 450 MPa by using a high pressure cell. It was indicated that the microviscosity showed a dramatic change in the vicinity of the phase transition point. The T vs. P phase diagram of methylcellulose aqueous solution was constructed, and it indicated that the melting point was an increasing function of pressure. In situ microscopic observation of pressure-induced gelation of methylcellulose aqueous solution was also performed with a microscope, and it could be seen that gel phase of the sample disappeared and sol formed gradually. Pressure-released study by fluorescence measurement also showed that the phase transition of MC solution was reversible.

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1. Introduction

Cellulose is the most abundant polysaccharide, which consists of (1–4) linked β -D-glucopyranosyl monomers, and this configuration contributes to its rigid structure and to the formation of aggregates through intra- or inter-molecular hydrogen bonds via hydroxyl groups [1]. Temperature-induced gelation of aqueous solutions of macromolecules has been attributed to the formation of a three-dimensional crosslinked network structure, and thermoreversible gels formed on cooling or heating have been studied extensively [2]. Haque and Morris studied the gelation of methylcellulose by rheology, differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) and optical rotation (OR), and proposed that methylcellulose chains exist in solution as aggregated bundles, and the ends of the bundles come apart on heating, exposing methyl groups to the aqueous environment. When the temperature increased, the methyl substituents shed structured water, and form a hydrophobically crosslinked network [3]. Yuguchi et al. studied the gelation of methyl hydroxyl propylcellulose by DSC and X-ray small angle scattering and found a similar result as Haque et al. for methylcellulose [4]. The gelation of methylcellulose with different molecular weights was studied by small deformation oscillation rheological measurements and DSC, and it was found that the

gelation was promoted by the increase in molecular weight of MC: the elastic modulus became larger, the gelation occurred at lower temperatures and the DSC peaks accompanying the gel–sol transition became sharper [5]. Kobayashi et al. studied the thermoreversible gelation of methylcellulose in aqueous solution by static and dynamic light scattering (DLS), small-angle neutron scattering (SANS), and rheology. Both the network formation process and the gel structure were examined in details. Semidilute solutions exhibit two relaxation modes in DLS: one reflecting cooperative diffusion and the other attributable to pregel clusters [6]. Funami et al. investigated the thermal aggregation of methylcellulose with different molecular weights in an aqueous system by static light scattering technique to trace the transition of its molecular size and shape upon heating. Temperature-dependence of some rheological parameters was also examined to make a bridge between the macroscopic changes of methylcellulose and its molecular transition during thermal gelation [7]. Rinaudo and Desbrieres discussed the properties and mechanism of methylcellulose solution in detail, and they thought that the mechanism of gelation is described as a two step process in relation with the existence of trimethylated glucose zones necessary to get the first clear loose gel (35 °C < T < 60 °C), and the second step is a phase separation occurring around 60 °C with the formation of a turbid strong gel [8]. Takahashi et al. investigated thermoreversible gelation and phase separation in methylcellulose solution, and applied the modified Eldridge–Ferry method to their experimental data on the sol–gel transition. The results indicated that the junction shape

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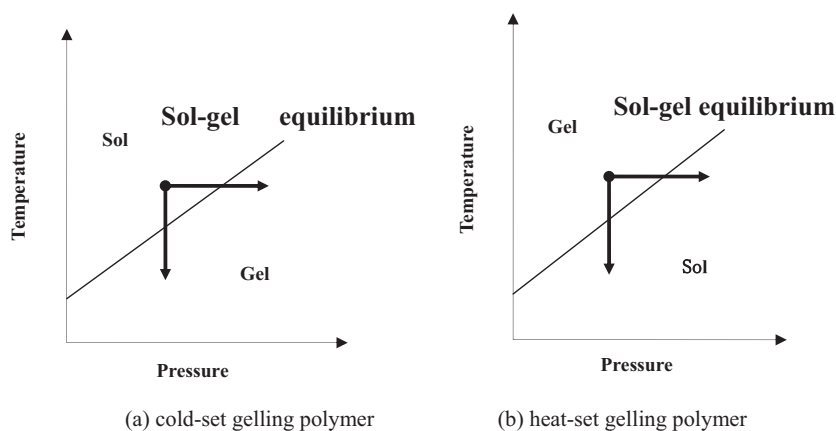


Fig. 1. The schematic drawing of sol-gel phase diagram for a gelling polymer.

in methylcellulose gel took thin, rodlike fringed-micellar crystallites, and the phase diagram of methylcellulose solution showed the co-occurrence of gelation and phase separation [9,10].

Until now, for the gelation of MC in aqueous solution, three possible intermolecular interactions were reported: (1) hydrogen bonding between unmodified hydroxyl groups on cellulose chains, (2) hydrogen bonding between hydroxyl groups of cellulose and water molecules, and (3) intermolecular hydrophobic association between the methyl groups on the MC molecules [11,12]. The interplay of these interactions dictates the mechanism of thermoreversible gelation. Especially, hydrophobic association of MC becomes pronounced at elevated temperatures when the hydration cage-like structures around hydrophobic parts of the MC molecules start to collapse yielding in considerable entropic contribution. This process of gelation was therefore found to be entropy-driven [13–16].

Fig. 1 shows a schematic drawing of compression and cooling, which implies that there are two ways about gelation of soft matter. The conventional method is cooling(heating), in fact, the other effective way is compression(decompression). In other words, compression is equivalent to cooling in the way of melt solidification, which can also overcome the limit of thermal conductivity. Since 1972, several papers have described the influence of high pressure on the gelation of methylcellulose aqueous solution. Suzuki studied the pressure effect on the sol-gel transition of methylcellulose solution by falling ball method, and Eldridge-Ferry plot was carried out to estimate the enthalpy of gelation ΔH [17]. Hayashi and Hayashida found that pressure treatment at about 500 MPa could modify the properties of these soft matters [18]. Stute et al. found that differences in properties between pressure- and temperature-induced gels can be observed [19]. To put these materials effectively to practical use, it is necessary to know how these properties are affected by pressure on a molecular scale. In addition, thermoreversible gels formed on cooling have been studied extensively, however, those formed on heating have not been understood so well. Therefore, to better understand the mechanism of gelation of soft matter, in the present paper, methylcellulose has been selected as a model sample, in situ heat- and pressure-induced gelation of methylcellulose aqueous solution has been studied by rheology and fluorescence measurement.

2. Experimental

The MC sample, with a commercial name of SM4000, was a gift from Shin-Etsu Chemical Co. Ltd. (Japan). The average molecular weight was 380,000 and the average degree of substitution was 1.8 [8]. The material was used as received without further purification.

MC samples were dispersed in distilled water, and dispersions were stirred for 24 h, and then transferred to a refrigerator at 4 °C and kept for at least 24 h prior to measurements.

Dynamic viscoelastic measurements were carried out using a RheoStress 600 (Haake, Thermo Electron, Germany) with a cone plate geometry. The exposed surface of the sample was covered with silicone oil to avoid evaporation of water in the solution, immediately after the sample solution was set between the plate and the cone. The temperature dependence of the storage (G') and the loss (G'') shear moduli was examined at a scan rate of 0.5 °C/min and at an angular frequency of 1.0 rad/s.

For fluorescence measurements, the fluorescence probe 9-(dicyanovinyl)-julolidine, DCVJ (Invitrogen, USA), was used as received, which is well-established as an indicator of solvent microviscosity. A sample-filled internal cell made of quartz (the optical path length was 5 mm) which had a section of stretch plastic tube was inserted in a stainless steel (JIS SKD-62) high-pressure cell with four sapphire windows sealed with o-rings and gasket rings, which was connected to a high-pressure pump (Hikari High Pressure Machinery, Hiroshima, Japan). The internal cell was compressed through the pressure medium of the silicone oil (Shin-Etsu Chem. Co. Ltd., Japan). The cell body had a tubelike flow channel, in which the constant-temperature water was circulated to maintain the temperature. The high pressure cell unit was set up in a dark chamber, and the excitation light with a wavelength of 435 nm from a Hg-Xe lamp (MUV-202U, Moritex Co., Japan) selected by a monochromator (ISA HR-320) was irradiated to the sample through the optical window of the cell. The fluorescence from the sample was collected by quartz lenses (focal distance = 100 mm and 40 mm) and analyzed by an Ocean Optics USB2000-FLG Spectrofluorometer (Ocean Optics, USA). Methylcellulose solutions were subjected to pressures up to 450 MPa at the temperature range from 25 °C to 75 °C by using a high pressure cell. The microviscosity η was calculated by $\log \Phi = C + x \log \eta$ [20], where Φ is the fluorescence quantum yield, C and x are constants (for DCVJ, x has been reported to be 0.6 [21]).

DSC was performed using a micro DSC-III calorimeter, Setaram Ltd., France. Approximately 800 mg of the sample solution and the equal amount of distilled water as a reference were hermetically sealed into each DSC pan. Cooling and heating DSC curves were recorded in the temperature range from 5 °C to 85 °C at a scan rate of 0.5 °C/min.

3. Results and discussion

Fig. 2 shows storage modulus G' and loss modulus G'' as a function of temperature in heating and cooling processes for a

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