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# **Physical Chemistry and Industrial Application of Gellan Gum**

Volume Editor:

K. Nishinari

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## Introduction

Gellan gum was first approved for food use in Japan in 1988. It had been used before the approval for culture mediums in microbiology and biotechnology. It has attracted much attention from food industries all over the world. It consists of a tetrasaccharide unit, glucose, glucuronic acid, glucose and rhamnose, and it forms a transparent gel which is heat-resistant in the presence of divalent cations. There have been many investigations of this gelling material; however, the mechanism of the sol–gel transition is not completely understood. Gellan gum is expected to be a good model for the study of thermoreversible sol–gel transitions because it dissolves well in water if it is converted into, for example, a sodium type, and it forms a transparent gel. In this sense, gellan gum is a better model sample than  $\kappa$ -carrageenan or agarose, which forms a gel but which is not so transparent in comparison to a gellan gum gel.

The collaborative research group was organised in the Research Group of Polymer Gels affiliated to the Society of Polymer Science, Japan, in 1989. The group consists of various laboratories with different disciplines: rheology, NMR, differential scanning calorimetry (DSC), light scattering, osmotic pressure, small-angle X-ray scattering, scanning tunnelling microscopy, etc. The first results of the collaborative research were presented at the annual meeting of the Society of Polymer Science, Japan, in 1991, and were then published as a special issue of *Food Hydrocolloids* 7:361–456 (1993). Since the common sample of gellan gum used in the collaborative research was essentially a potassium type (KGG-1) and contained some other cations such as calcium and magnesium in addition to sodium ions, it was difficult to dissolve even if heated to 100 °C. It was impossible to determine the molecular weight of the common sample by light-scattering and osmotic pressure measurements. Therefore, Profs. E. Ogawa and K. Kubota changed the common sample into a tetramethyl ammonium type, and performed the osmotic pressure and light-scattering measurements, and ob-

tained molecular weights of  $M_n = 5 \times 10^4$  and  $M_w = 2.4 \times 10^5$ , respectively. The purpose of the collaborative work is to use the common sample in all the laboratories with different techniques so that we can compare the experimental results directly. Unfortunately, for the first sample this aim was not realised because of the poor solubility of the sample.

I was lucky to ask to Dr. Sanderson of Kelco Ltd. to prepare the sodium-type gellan sample. His team was so kind to prepare a sodium-type gellan gum (NaGG-2), and I could distribute the common sample to our collaborative members in 1992. The results of the second collaborative research were presented at the International Workshop on Gellan Gum and Related Polysaccharides held in Osaka in 1993. The papers of this collaboration together with some other interesting papers on gellan from the laboratories of Prof. E.R. Morris, Prof. M. Rinaudo and Dr. A. Nussinovitch were published in the special issue of *Carbohydrate Polymers* 20:75–207 (1996). However, the common sample used in our collaborative research group was not completely converted into a sodium type, and, therefore, osmotic pressure and light-scattering measurements were performed again for the ion-exchanged sample by Profs. E. Ogawa and K. Kubota. Unfortunately, the sample used was different from the second common sample, NaGG-2.

I could not give up the dream to understand better the sol–gel transition of this polysaccharide, and again asked San-Ei Gen F.F.I. Inc. to prepare the better sample. Dr. Sanderson was generous to teach the method of preparing the sodium-type gellan gum to Drs. I. Asai and T. Omoto of San-Ei Gen F.F.I. Inc., and they prepared a sodium-type gellan gum (NaGG-3). The important difference between the second common sample, NaGG-2, and the third common sample, NaGG-3, is that it was possible to do the light-scattering and osmotic pressure measurements for the latter without further treatment. The weight-average molecu-

lar weight was determined by Professor Kubota to be  $9.5 \times 10^4$ , and the number-average molecular weight was determined by Professor Ogawa to be  $5.8 \times 10^4$ . The sample was distributed to our group members in 1997. The experimental results were presented at the Osaka City University International Symposium 98 – Joint Meeting with the 4th International Conference on Hydrocolloids (OCUIS98-4ICH) in October 1998. During the conference, an informal meeting was held. In addition to our Japanese group members Dr. V.J. Morris, Prof. E.R. Morris, Prof. M. Rinaudo, Prof. M. Dentini, Dr. S. Kasapis, Dr. Sworn and Dr. Morrison attended the meeting, and discussed further collaboration.

The present special issue consists of 19 papers contributed by these participants. The first paper describes the characterisation of gellan gum using laser light scattering by Professor Kubota in collaboration with Professor Nakamura. Professor Kubota is an expert in dynamic light scattering using his home-made apparatus, and he could determine the radius of gyration and the weight-average molecular weight of the common sample. The second paper describes the osmotic pressure measurements by Professor Ogawa, who has been studying the solution properties of polymers using this method for a long time. She could determine the number-average molecular weight and the second virial coefficients of the common sample as well as for the further-cation-eliminated sample. The third paper is from the laboratory of Professor Watanabe. The molecular forces responsible for gel formation are believed to be mainly hydrogen bonds, and her group presents an interesting discussion on this problem using results from NMR and circular dichroism (CD) studies. The fourth paper is a contribution from the team of Dr. Annaka in collaboration with Dr. Tokita, and discusses the gel–sol transition using multinuclear NMR. Professor Tsutsumi introduces an interesting method to study the sol–gel transition using electron spin resonance spectroscopy (ESR) (paper 5). Manganic ions were added to gellan gum solutions since manganic ions are active in ESR. Although the effects of divalent cations such as calcium and magnesium on the gelation of gellan gum are reported in papers 3, 8, and 11, the effects of manganic ions are only reported in paper 5. Dielectric relaxation was observed by the time-domain reflectometry method by Dr. Shinyashiki (paper 6). His team discusses the state and motion of water based on this method. Small-angle X-ray scattering measurements and the conformational analysis were performed by the team of Professor Kajiwara in collaboration with Dr. Kitamura (paper 7). Professor Kajiwara has been using this method for more than 10 years, and succeeded in working out the structure and conformation of this polysaccharide. The team of Professor Izumi carried out DSC and X-ray studies over the wide range of concentrations, and proposed a phase diagram (paper 8).

Prof. K. Nakamura has been studying the sol–gel transition of polymers based on rheology, and he clarifies the viscoelastic behaviour using small-deformation oscillatory measurements and sound velocity measurements with Professor Kubota in paper 9. Dr. Takigawa has been interested in the rheological behaviour of gels for a long time, and performed measurements to clarify the nonlinear shear-rate-dependent behaviour of gellan gum solutions (paper 10). In our laboratory, small-deformation oscillatory measurements and DSC have been used to study the rheological and thermal properties and the sol–gel transition. The shift of the DSC exothermic peak in cooling DSC curves to lower temperatures by more than 4 °C in comparison to the sodium-type gellan gum sample (NaGG-2) surprised us at first, and we felt the importance of the sample purification (paper 11). We also studied the effects of sugars on the sol–gel transition by rheology and DSC (paper 12). A further ion-eliminated sample was prepared in the laboratory of Professor Watanabe from the potassium-type gellan (KGG-1) which was used in the first collaborative research, and was studied to clarify the gelation mechanism by CD (paper 13). The phase transition is discussed by Professor Hatakeyama based on data on transition temperatures mainly for the first collaborative sample, i.e. potassium-type gellan (KGG-1) (paper 14).

Dr. V.J. Morris attracted much attention in his stimulating lecture showing beautiful atomic force microscope (AFM) photographs at OCUIS98-4ICH. His paper (15) is a challenging paper proposing a fibrous model based on this AFM observation. Professor E.R. Morris, a world-famous pioneer in the field of thermoreversible sol–gel transitions, contributes paper 16, which describes the effects of sodium ions on the rheological behaviour of deacylated gellan. The effects of sugars on gels are important in relation to making dessert jellies. Drs. Kasapis and Sworn used rheological data to demonstrate the transformation of the gellan network from an enthalpic highly aggregated gel to an entropic lightly crosslinked arrangement with increasing levels of sugar (0 to 85%). These undergo readily vitrification and are of importance to the confectionary industry (paper 17). Dr. Asai has been working for a long time on the application of polysaccharides in food industries, and his group describes some new applications of gellan gum in paper 18. The final paper is written by Dr. Morrison's group. It reports an interesting trial to use gellan as a gelatin alternative.

I tried to gather together all the data and make a comparison of the transition temperatures of gellan gum solutions as a function of the concentration of gellan gum, and of the added salts or sugars, etc. However, the exchange of this information and the rewriting of the manuscripts by each author took such a long time, and now I think it better to send all our papers to the

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publisher and ask readers to compare all these data by themselves. I believe that papers 1-13 used the same common sample, NaGG-3, and so we can compare the experimental results directly.

It is a great pleasure for me to include papers which describe the application of gellan gum in the food industry.

I hope that some discussions, questions and comments attached to each paper will be interesting and helpful for readers to achieve a better understanding.

Finally, I would like to thank all the contributors, and especially Prof. E.R. Morris for his corrections of English and comments for papers written by Japanese authors, and Profs. K. Ogino, T. Nishi and I. Ando for their valuable comments on manuscripts.

K. Nishinari

Takahashi R, Akutu M, Kubota K, Nakamura K:	Characterization of gellan gum in aqueous NaCl solution . . . . .	1
Ogawa E:	Temperature dependence of the conformational properties of sodium-type gellan gum in aqueous solutions . . . . .	8
Matsukawa S, Tang Z, Watanabe T:	Hydrogen-bonding behavior of gellan in solution during structural change observed by <sup>1</sup> H NMR and circular dichroism methods . . . . .	15
Annaka M, Honda J-I, Nakahira T, Seki H, Tokita M:	Multinuclear NMR study on the sol–gel transition of gellan gum . .	25
Tsutsumi A, Ozawa T, Okada M, Hiraoki T, Ishii F:	Electron spin resonance study on the sol–gel transition of gellan gum aqueous solution by the addition of paramagnetic metal- ions . . . . .	31
Shinyashiki N, Sakai T, Yamada G, Yagihara S:	Dielectric study on the dynamics of an aqueous solution of gellan gum . . . . .	36
Yuguchi Y, Urakawa H, Kitamura S, Wataoka I, Kajiwara K:	The sol–gel transition of gellan gum aqueous solutions in the presence of various metal salts . . . . .	41
Izumi Y, Saito S, Soma K:	Differential scanning calorimetry and structural studies of the sol–gel transition of gellan gum in water . . . . .	48
Akutu M, Kubota K, Nakamura K:	Light scattering, sound velocity and viscoelastic behavior of aqueous gellan solutions . . . . .	56
Takigawa T, Nakajima K, Masuda T:	Rheological properties of the gellan /water system . . . . .	62
Miyoshi E, Nishinari K:	Rheological and thermal properties near the sol–gel transition of gellan gum aqueous solutions . . . . .	68
Miyoshi E, Nishinari K:	Effects of sugar on the sol–gel transition in gellan gum aqueous solutions . . . . .	83
Matsukawa S, Huang Z, Watanabe T:	Structural change of polymer chains of gellan monitored by circular dichroism . . . . .	92
Hatakeyama T, Nakamura K, Takahashi M, Hatakeyama H:	Phase transitions of gellan–water systems . . . . .	98
Morris VJ, Kirby AR, Gunning AP:	A fibrous model for gellan gels from atomic force microscopy studies . . . . .	102
Morris ER, Richardson RK, Whittaker LE:	Rheology and gelation of deacylated gellan polysaccharide with Na <sup>+</sup> as the sole counterion . . . . .	109
Sworn G, Kasapis S:	Molecular origins of the rheology of high-sugar gellan systems . . . .	116



---

Omoto T, Uno Y, Asai I:	The latest technologies for the application of gellan gum . . . . .	123
Morrison NA, Sworn G, Clark RC, Chen YL, Talashek T:	Gelatin alternatives for the food industry . . . . .	127
	<b>Contents of Volume 114</b>	
	Author/Title Index . . . . .	133
	Key Word Index . . . . .	135