

Light-Scattering Study on Thermoreversible Gelation in Biological Polysaccharides

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Relaxation of aqueous κ -carrageenan solutions and gels has been studied by dynamic-light scattering. Broad distributions of the relaxation times observed at the gel point as well as in the gel phase were analyzed in terms of a stretched-exponential function rather than a power-law formula employed frequently. A hierarchically constrained dynamics model, which underlies the stretched-exponential function, is proposed to represent the dynamics of the gel network.

INTRODUCTION

Gelation has attracted much interest in the past decade. The interest stems from the recognition that gelation is a new kind of critical phenomena which is related to the divergence of the connectivity length associated with the network formation.

The point of gelation is identified macroscopically by the loss of fluidity, or alternatively, by the onset of rigidity of the medium. On the other hand, microscopic aspects of gelation can be obtained by scattering measurements. The formation of polymer network imposes mechanical constraints on the motion of an individual segment, which bring about changes in the relaxational properties of thermal fluctuations.

There has already been a number of publications on the dynamic light-scattering experiments on gelation. In most of these studies, the heterodyne correlation function, or the dynamic structure factor at and around the gel point has been found to fit well to a power-law decay. This is usually related to the spatial fractal-like structure which develops at the gel point. Thus, the development of power-law decay seems to be a universal feature of the gelling polymer systems. However, in many systems, the power-law decay persists after the gel is formed. This cannot be interpreted by a fractal-cluster-diffusion model.

In this regard, it should be noted that a stretched-exponential relaxation can also be derived from fractal time set brought about by the spatial fractal structures. Then, it may be possible that the correlation function at and around the gel point can be explained in a unified

unified fashion by a stretched-exponential decay, not by a combination of power-law and stretched-exponential functions.

In the present work, we have measured the dynamic-light scattering spectra from marine polysaccharide κ -carrageenan at and around the gel point. We have tried to fit the correlation functions to both power-law and stretched exponential formulae. The qualities of the fit to these different functions are compared, and the physical meanings behind these formulae are argued.

EXPERIMENTALS

Samples were aqueous solutions of κ -carrageenan and the corresponding gels. Reagent grade κ -carrageenan (Wako Chemicals Co.) was dissolved in deionized, and distilled water at 70°C, and dialyzed for two days to remove impurities. Then, the solution was filtered with a Millipore filter of 0.2 μ m pore size, followed by freeze-drying. The concentration of aqueous pre-gel solution was adjusted to 4.75 wt%, which was poured into a cylindrical glass cell of 20mm diameter.

Apparatus used to measure dynamic light-scattering was ALV-5000 correlator, goniometer, and photon-counting detection systems. Light source was a semiconductor-pumped solid-state laser operated at 532 nm with an output of 30 to 100 mW depending of the scattering power of the sample. The scattering angle was kept constant at 90°. Temperature stability of the sample was better than $\pm 0.2^\circ\text{C}$.

Although the scattering intensity depended on position in the gel phase due to static inhomogeneity, ensemble averaging was not pursued in

the present study. Thus, our measurements are on time-averaged quantities from a single scattering volume of the sample.

RESULTS

Two sets of dynamic light-scattering measurements were made in the present study. One was the measurement of the temperature dependence of the equilibrium correlation function around the gel point, and the other the measurement of the evolution of the correlation function as sol-gel transformation proceeded at the gel point.

First, the correlation function was measured at each temperature on cooling from 35 to 23°C with 1°C interval. In each measurement, the sample was kept at constant temperature at least 12 hours before the measurement to assure equilibration. The result is shown in Fig.1. It is seen that the drastic change in the shape of the correlation function $g^{(1)}(t)$ occurs between 32 and 33°C. Thus, we identify the gelation temperature of our sample to be 32°C.

Next, the evolution of $g^{(1)}(t)$ as the gelation reaction proceeded at the gelation temperature is given in Fig.2. The origin of elapsed time t_e is chosen at which the temperature of the gel is changed from 33 to 32°C. It is seen that a drastic change of the shape of $g^{(1)}(t)$ occurs between $t_e = 1830$ and 1950 seconds. The corresponding change in the scattered intensity $I(t_e)$ is shown in Fig.3. A large and nearly discontinuous change in $I(t_e)$ is clearly seen around $t_e=1940$ seconds. Thus, we may conclude that gelation took place at this elapsed time.

DISCUSSION

According to the previous publications, coexistence of a power-law and a stretched-exponential-type decays seems to be a general feature observed in light-scattering spectra around a gel point.¹⁻⁷

Martin et al.^{1,2} studied closely methanol solution of tetramethoxysilicon by light-scattering at and around the gel point. They analyzed their experimental results by cluster-diffusion model, which assumes a fractal set of clusters of all sizes, from monomers to an infinite network, will be present just at the gel point. Since the diffusion constant of clusters will depend inversely on their sizes, the dynamics at the gel point is dominated by an infinite series of relaxation times, which leads to a power-law relaxation of the light-scattering correlation function.

On the other hand, the cluster-diffusion model is irrelevant below the gel point, i.e., in the gel

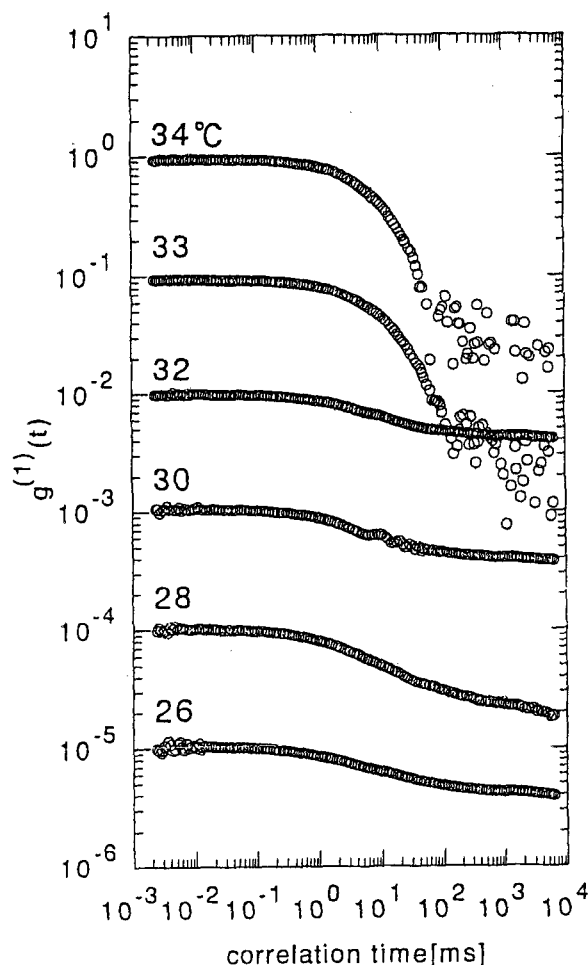


Fig.1 Correlation function $g^{(1)}(t)$ at each temperature. The scale on the ordinate is for the curve at 34°C. The other curves are displaced downward by an order of magnitude for clarity.

phase, because almost all the existing polymer chains will be incorporated in a single network.

In fact, their experimental results show that the form of the correlation function in the gel phase is essentially the same as that observed at and just above the gel point except that the amplitude of the correlation function decreases. Thus, the cluster-diffusion model cannot explain the reason why the power-law relaxation is observed not only at the gel point but also throughout the gel phase.

Ren et al.^{3,4} made light-scattering measurements on aqueous gelatin solutions and gels, and observed three different modes of relaxational behaviors depending on the time scales involved. In a short-time limit, the dynamics is controlled by a collective diffusion of the polymer chains (gel mode). In an intermediate-time region, a power-law relaxation appears, which is truncated by a stretched exponential relaxation in a long-time limit. These characteristics are

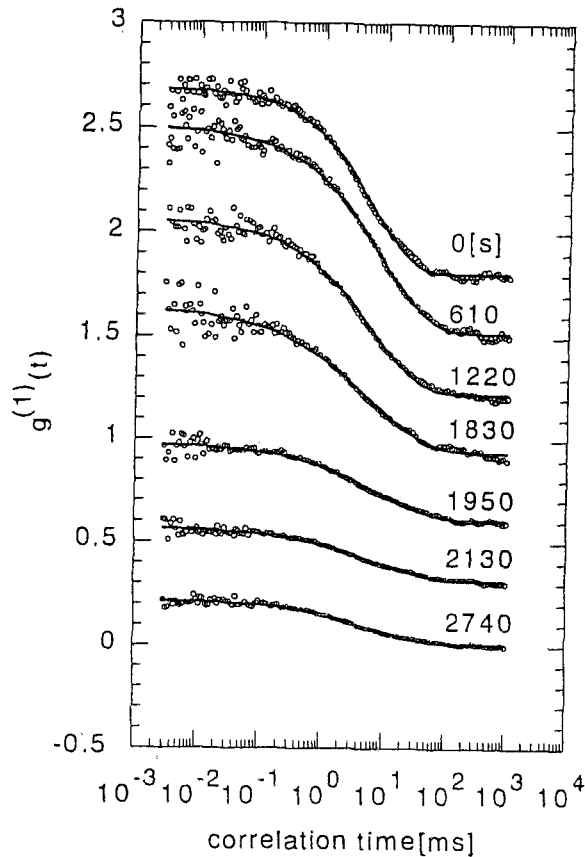


Fig.2 Correlation function $g^{(1)}(t)$ at the gelation temperature, 32°C, as a function of elapsed time. The origin of elapsed time is the instance at which the temperature is changed from 33 to 32°C. The scale on the ordinate is for the curve at 0 s. The other curves are displaced downward appropriately for clarity. Solid lines are best fit to an stretched exponential function.

essentially the same as those observed by Martin et al. in both above and below the gel point. They interpreted their results in terms of an analogy with α - and β -relaxation in glasses. Although this analogy is attractive, a real physical picture behind the observed anomalous relaxation is still unclear, as they themselves admitted.

On considering relaxation in gels, we have to bear in mind that the very broad distribution of relaxation times is not a universal feature of gels. For example, light-scattering spectra from some chemical gels, e. g., acrylamide and related gels, show nearly single exponential decay, which has been interpreted in terms of a collective diffusion of polymer segments. This mode is frequently observed not only in gels but also in polymer solution, and is called gel mode.

The point is, therefore, that in some gels only the gel mode is observed, while in other gels an extremely broad distribution of relaxation times

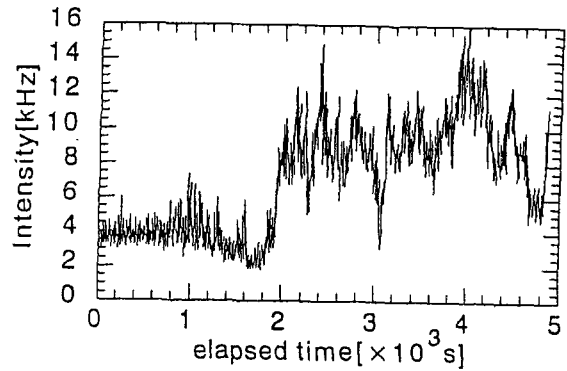


Fig.3 Scattering intensity at 32°C as a function of elapsed time.

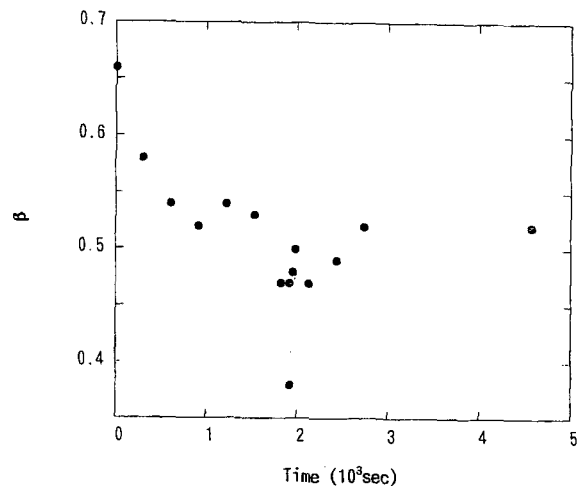


Fig.4 The shape parameter β obtained from the fit shown in Fig.2

dominates the relaxational behavior. In the latter case, the gel mode seems to be still present but is of minor importance. The cause of these apparently different characteristics of gels is still unsolved, though it is conceivable that the network structure of respective gels is crucial in determining their relaxational behaviors.

Now, turning attention to our experimental results, we see that the relaxation in κ -carrageenan is characterized by a broad slow mode as has been observed in gelatin, tetramethoxysilicon and other polymeric systems. We tried to fit our data to a power-law or stretched-exponential functions as has been done in previous studies. We preferred to fit our data in the whole time region to a single function, rather than fitting the different time regions separately, as has been done in most previous studies.¹⁻⁴ The fitting equations we tried are as follows.

$$C(t) = A \exp(-t/\tau_1) + B(1+t)^{-\alpha} + C \exp[-(t/\tau_2)^\beta] \quad (1)$$

$$C(t) = D + E \exp[-(t/\tau_0)^\beta] \quad (2)$$

Here, A, B, C, D, E, α , β , and τ 's are constants.

In the sol phase, the correlation function could be fitted quite satisfactorily to Eq(2) with D=0. In the gel phase, satisfactory fits were obtained both with Eq(1) and Eq(2) (D \neq 0). Although the quality of the fit was slightly better with Eq(1) than with Eq(2), it is natural considering that the number of fitting parameters are seven in Eq(1) as compared with three in Eq(2). At any rate, the difference between the qualities of the fit was not significant. Thus, the use of Eq(2) was preferred, because this allowed us to use the same fitting formula over the whole temperature and time ranges.

The results of fitting to Eq(2) are shown in Fig.2 as solid lines. The change of β with time is depicted in Fig.4. It is seen that β becomes minimum at the gelation point, showing that the distribution of the relaxation time becomes broadest there.

The stretched-exponential formula shown in Eq.(2), which is also called the Kohlrausch relaxation law, is known to fit quite well to a wide range of relaxation phenomena.⁸ Sometimes, the use of this formula has been criticized on the ground that the mechanism underlying this formula is unclear. However, there are some cases where this formula can be derived from a fairly rigorous theoretical model. One such example is a hierarchically constrained dynamics (HCD) model, which, in the authors' view, may be applied to gels. The model can be outlined as follow.

We assume that various degrees of freedom (DOF) in the system can be classified according to their relaxation times, from fast to slow. Thus, DOF with the fastest relaxation time constitute DOF level 1, those with the next fastest constitute DOF level 2, and so forth. DOF belonging to different levels relax in series, not in parallel, such that DOF in level n can relax only after DOF in level n-1 has relaxed. In other words, faster DOF successively impose constraints on the motion of slower DOF. This is the formal structure of HCD model.

Some swollen gels may be a good example of HCD model. The fastest motional unit should be a single atom or a small group of atoms in a side chain. The next fastest may be a group of the fastest unit or a larger side chain, which will be followed by some group of side chains, a sub-chain, and so forth.

According to the theoretical study on a spin version of HCD model,⁹ the parameter β in Eq.(2) is related to a depth of the hierarchy. The deeper is the hierarchical structure, the smaller is β . We see in Fig.4 that β is minimum at the gel point. This is consistent with the view that nearly infinite self-similar structure of clusters will set in at the gel point. In the gel phase, β becomes larger than the value at the gel point, but it is sufficiently smaller than the value in the sol phase. This indicates that the crosslinks between chains impose additional constraints on the slow motion of the chains, thus enhancing the hierarchically constraint structure as compared with the sol phase..

We admit that our idea to apply HCD model to dynamics of gels is speculative at present. According to the theoretical study⁹, a rich variety of dynamical behaviors can be predicted from this model according to parameters related to a system structure. To test the validity of our idea, it will be necessary to study closely the connection between dynamics and the network structure of respective gels, and on the basis of these studies, to make a detailed comparison between theory and experiment.

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