# Spinodal Decomposition and Syneresis of PVA Gel

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ABSTRACT: The phase separation of a network in the unstable region has been investigated using a homogeneous transparent poly(vinyl alcohol) (PVA) gel by volume and UV transmittance measurements as well as by time-resolved light scattering measurements. It was found that the light scattering intensity $I(Q)$ shows a single peak which increases in intensity exponentially with time without shifting the peak position in the early stage of phase separation, suggesting that a spinodal decomposition (SD) type phase separation occurs in this system. In contrast to the usual fluids, the domain growth is extremely slowed down in the late stage because the elastic force of the gel suppresses the surface tension force, which is the driving force of domain growth. This is the so-called pinning effect. As the SD approaches the end, the UV transmittance of the gel increases gradually and the scattering intensity decreases during the shrinking process of volume (syneresis), which corresponds to a relaxation process of the microscopic internal fluctuations produced in the SD process.

## Introduction

Polymer gels are three-dimensional networks swollen with solvents, which are elastically soft, very impact-resistant, highly solvent-absorptive, and so forth; these features are utilized in many applications such as shock absorber, water absorber, acutator, biosensor, living space of useful bacteria, and contact lens.[1−5] Poly(vinyl alcohol) (PVA) gel is of great interest from both scientific and industrial viewpoints. Scientifically, it is a normal physical gel whose cross-linking points are crystallites, and its phase behavior,[6−10] structure,[11−14] formation process,[15−19] and melting and regelling[20] have extensively been studied. Hyon et al.[21] reported that the PVA gels formed in mixtures of dimethyl sulfoxide (DMSO) and water show some interesting features, depending on the mixing ratio of DMSO and water. In a mixture of DMSO and water with a volume ratio 60/40, the gelation rate is very fast compared with those of other ratios, and the resultant gel is opaque at room temperature (25 °C). On the other hand, in a mixture of a ratio 80/20, the rate is very slow, and the transparent gel is obtained at room temperature. In a series of studies,[8,13,14,16,19,22,23] we have therefore investigated the structure and the formation processes of the PVA gels formed in mixtures of DMSO and water and pointed out that spinodal decomposition (SD) type liquid−liquid phase separation plays an important role in the formation process. During these studies, we found that when the homogeneous PVA solution in a mixture of the ratio 60/40 is quenched to a temperature below −20 °C, it becomes a transparent gel. However, when it is kept for a long time, e.g., several days or several weeks, it gradually becomes translucent, depending on temperature. This result suggests that a phase separation occurs in the transparent PVA gel.

Most studies on PVA gels including our studies are concerned with their formation processes. As pointed out by de Gennes,[24] we need two kinds of statistical information to understand a gel. One is information about the situation at the moment of preparation, and the other is about the situation at the moment of study (solvent, temperature, etc.). Thus, gels must be described in terms of two ensembles: the “preparative ensemble” and the “final ensemble”. It is evident that our previous studies are related to the “preparative ensemble” while a study on the phase separation of a gel after the gelation completed is obviously related to the kinetics from the “preparative ensemble” to the “final ensemble”. In this sense, the studies on phase separation of a gel network are much different from those on the formation process.

Phase separation of a gel is one of the unsolved problems in soft-matter science as well as polymer science although some pioneering works were done by several researchers. Experimental work on phase separation of gels was reported by Hirotsu et al.[25] on *N*-isoporpylacrylamide (NIPA) gel in water. When a swollen NIPA gel is suddenly brought into another state in the two-phase or one-phase region by a temperature jump, it becomes opaque without any appreciable volume change, suggesting that spinodal decomposition (SD) occurs in both the cases. Theoretically, de Gennes[26] generally discussed polymer gel and its SD, and a simulation work by Sekimoto et al.[27] first showed that a spongelike domain structure is produced by SD in a two-dimensional model gel. Recently, Onuki and Puri[28] have constructed a Ginzburg−Landau model for gels undergoing spinodal decomposition and showed that in the late stage the SD growth rate is slowed down due to the resistance of elastic forces of the gel network.

In this work, we have investigated structural evolution of a homogeneous transparent PVA gel when it was brought into the unstable state. The transparent PVA gel was prepared by quenching a homogeneous PVA solution in DMSO/water (60/40) at 100 to −40 °C. Though the gel is in the unstable state at −40 °C, the phase separation hardly proceeds within a usual laboratory time because of very low molecular mobility. Hence, we have observed the time dependence of the volume and transparency of the gel after a temperature jump to 25 °C. In addition, time-resolved light scattering measurements have as well been carried out to see the microscopic structural formation. The results will be discussed focusing on the phase separation as well as shrinkage (syneresis) of the gel.

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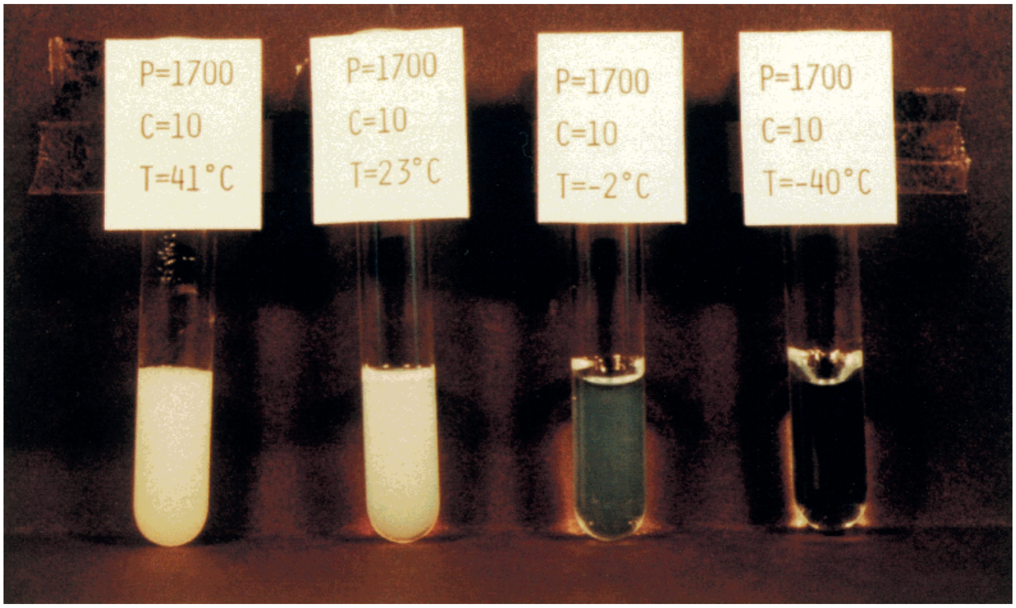

**Figure 1.** Photograph of PVA gels in a mixture of DMSO and water with a volume ratio 60/40 obtained by quenching to 40, 23, −2, and −40 °C. The PVA concentrations are 10 g/dL for all the gels.

## Experimental Section

**Materials.** Fully saponified atactic poly(vinyl alcohol) (PVA) with a number-average degree of polymerization $P_n = 1700$ and a molecular weight distribution $M_w/M_n = 1.97$ was used for the experiments. The details of characterization of the PVA sample have been reported elsewhere.[8] This PVA was dissolved in a mixture of dimethyl sulfoxide (DMSO) and water ($H_2O$) with a volume ratio 60/40 at about 130 °C to be homogenized in a glass tube. The homogeneous solution was transferred into a UV cell 1 × 1 cm in size for measurements of volume change and UV transmittance change. For the light scattering measurements, the solution was filtered through a 0.22 $\mu$m Millipore filter in a dust-free cylindrical Pyrex cell with an inner diameter 10 mm. After being homogenized again at 100 °C the solution was quickly quenched to −40 °C and allowed to stand for 24 h for gelation, resulting in a transparent gel. In this work, the PVA concentration was 5 g/dL for UV transmittance, volume, and light scattering measurements and 10 g/dL for a photograph to demonstrate the transparency of the gels.

**Measurements.** Light scattering (LS) measurements were carried out with System 4700 of Malvern Instruments Inc. using $Ar^+$ laser ($\lambda = 488$ nm, 75 mW) as a light source. The length of scattering vector $Q = 4\pi n \sin \Theta/\lambda$ , $n$ being reflective index, is in a range of $3.6 \times 10^{-4}$–$3.4 \times 10^{-3}$ Å$^{-1}$. The absolute intensity (Rayleigh ratio) was calculated using toluene as a standard to be $R_{tol} = 3.96 \times 10^{-5}$ cm$^{-1}$ for $\lambda = 488$ nm at $T =$ 25 °C.[29] To reduce the effect of inhomogeneity (speckle) of samples,[30] which arises from the gel structure itself, the measurements were mainly performed by rotating a sample cell at a frequency of 0.5−5 rpm. Time-resolved LS measurements were carried out just after transferring the transparent gel to a sample cell holder, which had been kept at 25 °C.

UV transmittance of the gel samples at wavelength 488 nm was recorded with time after the temperature jump from −40 to 25 °C using a double-beam spectrometer (Hitachi-220). The measurements were carried out under dry nitrogen atmosphere to avoid surface frost.

## Results and Discussion

**Transparent and Opaque PVA Gels: Quenching Temperature Dependence.** To clarify the present experimental situation, we first summarize some experimental results on PVA gels in a mixture of DMSO and water with a volume ratio 60/40.[8,19] Using this solvent, we can obtain both transparent and opaque gels by changing the quenching temperature as seen from photographs in Figure 1. The gels obtained by quenching to temperatures above about −20 °C are opaque, and the degree of the transparency increases with decreasing temperature. Below about −20 °C, on the other hand, the gels become transparent. These results were explained as competitive processes between the gelation and the liquid−liquid phase separation. The PVA solutions in DMSO/water (60/40) have a UCST type phase diagram with a critical temperature about 70 °C although the exact phase diagram is difficult to construct because the phase separation and the gelation occur simultaneously in the solution. When a PVA solution at 100 °C is quenched to a temperature above −20 °C, the spinodal decomposition (SD) type liquid−liquid phase separation occurs before gelation. Then, the cross-linking points are formed in the polymer-rich phase due to crystallization. It was found that the kinetics of the SD type phase separation is well described by the Cahn−Hilliard theory[31,32] in the early stage before gelation while the growth rate is slowed down due to the network formation or the so-called pinning effect.[19] On the other hand, the PVA gels obtained below −20 °C are transparent. Is the solution in a one-phase region? The answer is of course “no”. Below about −20 °C, the rate of crystallization is so fast that the network formation occurs in the homogeneous solution before the liquid−liquid phase separation initiates, resulting in a transparent gel. In other words, the final structure is kinetically determined by the competition between the liquid−liquid phase separation and the gelation. During these experiments, we found that the transparent gels produced below −20 °C becomes translucent and shrinks very slowly in several days or several weeks, depending on temperature. This suggests that the PVA gel is in a two-phase region or in an unstable region, and hence phase separation is expected to occur.

Even though the gel is in the unstable region, the phase separation rate is extremely slow at −40 °C. To observe the phase separation of this transparent gel within normal laboratory experimental period, it was jumped up to 25 °C to accelerate the phase separation in this study.

**Phase Diagram of the PVA Gel.** To discuss the phase separation of the PVA gel in a mixture of DMSO and water 60/40 in volume ratio, we need the phase diagram. First, we briefly consider a general phase diagram of a polymer gel. It is usually discussed in terms of the free energy involving two contributions of the mixing of polymer gel and solvent and the elastic energy of polymer gels. The free energy based on the lattice model[26,33−35] is given by

$$F = kT[(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)] + \frac{3kT}{2n}\left[\left(\frac{\phi_0}{\phi}\right)^{2/3} - 1 - \ln\left(\frac{\phi_0}{\phi}\right)^{1/3}\right] \qquad (1)$$

where $\chi$ is the interaction parameter, $n$ is the degree of polymerization of the subchain between the cross-linking points, $\phi$ is the volume fraction of polymers in the gel domain, and $\phi_0$ is that of the initial state. The phase diagram can be calculated from the following conditions: the osmotic pressure $\Pi$ $(= (1/a^3)\phi^2(\partial(F/\phi)/\partial\phi)$, $a^3$ being the volume of a site in the lattice model) exerted on the gel is zero ($\Pi = 0$) for the volume equilibrium curve (swelling curve) and the coexistence curve, and the osmotic modulus $K$ $(= \phi(\partial\Pi/\partial\phi))$ for the spinodal curve is also zero ($K = 0$). Below the spinodal curve, the gel is in the unstable region so that a SD type phase separation of the gel takes place to separate into swollen and shrunken phases. This SD process occurs usually much faster than volume change (syneresis) because the thermal equilibrium is attained faster than the diffusion process of solvent. Hence, after the SD, the gel must shrink as a whole to be in the volume equilibrium state. Once attaining the volume equilibrium, the fluctuations produced in the SD disappear, and the gel becomes homogeneous.

The phase diagram of the PVA gel formed in a DMSO/water (60/40) mixture at −40 °C was experimentally determined by Ohkura.[36] This phase diagram is reproduced in Figure 2. In this experiment, the temperature of the system was gradually raised from −40 to 100 °C, and the transparency and the melting of the gel were observed. Note that desorption of solvent was not observed in the experiment. As seen from the figure, the clouding point at a polymer concentration of 5 g/dL, where the present experiment was carried out, was observed at around 75 °C although it slightly depended on the raising rate of temperature. This clouding point approximately corresponds to the coexistence curve of the PVA gel. As the present experiment was done at 25 °C, which is very much deep in the two-phase region, a SD type phase separation of the gel is expected.

**Changes of Volume and Transparency of the Gel.** The transparent PVA gels obtained at −40 °C was jumped up to 25 °C. This process indicated by an arrow in the phase diagram in Figure 2. Just after the temperature jump we started the volume measurement as a function of time. The observed time evolution of degree of swelling defined as a ratio of the volume $V$ to the initial volume $V_0$ is shown in Figure 3a. In the first 2 min no appreciable change of the volume is observed, but then the volume begins to decrease gradually and levels off at around 500 min, meaning that the gel is in an apparent volume equilibrium state after about 500 min. This process of volume change (syneresis) is also indicated by an arrow in the phase diagram. The volume ratio $V/V_0$ at the new equilibrium state is 0.55.

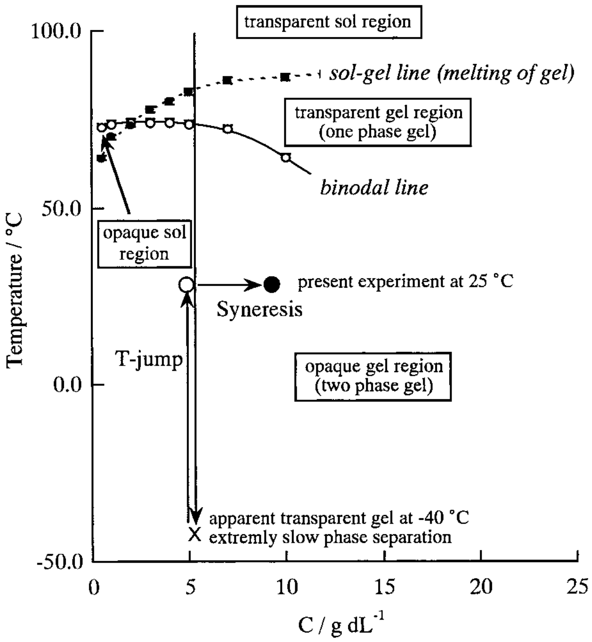

**Figure 2.** Phase diagram of PVA gel formed in a mixture of DMSO and water with a volume ratio of 60/40 at −40 °C.[36] In the phase diagram, × represents a position where the transparent gel was prepared; ○ and ● are the initial and final positions where the present experiment has been done.

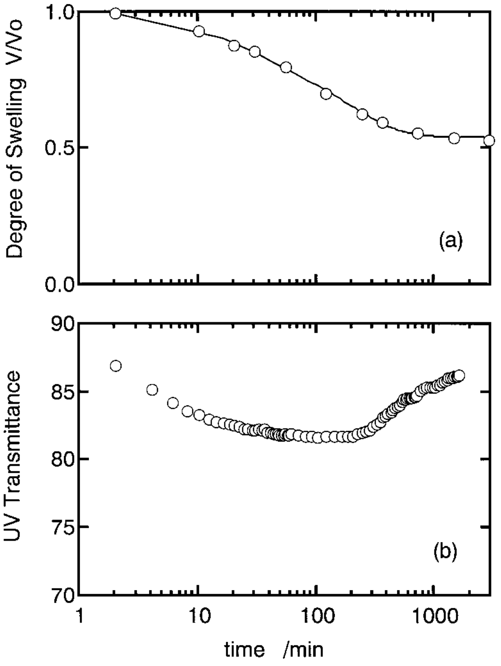

**Figure 3.** (a) Change of volume $V$ of the PVA gel formed in a mixture of DMSO and water with a volume ratio 60/40 at −40 °C after a temperature jump to 25 °C. Volume change is presented as a ratio to the initial value $V/V_0$. (b) Change of UV transmittance of the same gel as (a). The transmittance at the initial state was taken unity.

Under the same experimental condition, we measured the UV transmittance of the gel to see the transparency as a function of time after the temperature jump to 25 °C. The change of the transmittance is shown in Figure 3b where the data are corrected for the effects of volume change. In contrast to the volume change, the transmittance begins to decrease just after the temperature

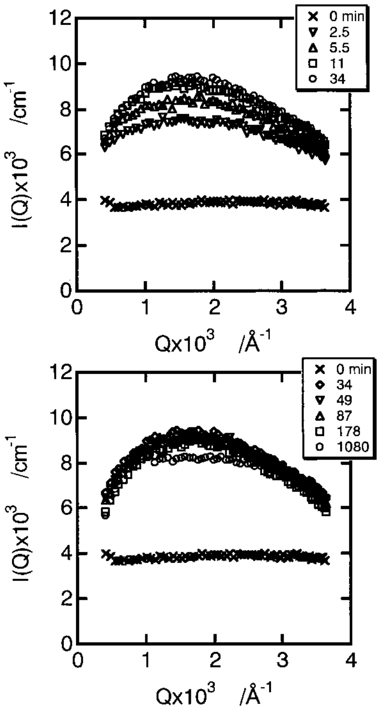

**Figure 4.** Time evolution of light scattering intensity $I(Q)$ of PVA gel formed in a mixture of DMSO and water (60/40) at −40 °C after a temperature jump to 25 °C: (a) from 0 to 34 min; (b) from 34 to 1080 min after the temperature jump.

jump, and it becomes 87% of the initial transmittance in 2 min. This suggests that the SD type phase separation occurs at 25 °C. Thereafter, it continues to decrease with time until about 30 min, but it levels off, keeping almost constant transmittance until 200 min though the volume continues to decrease. After that, the transmittance reversely begins to increase before the gel reaches an equilibrium swelling volume at ~500 min. The increase in transmittance implies that the internal structure of the gel becomes more homogeneous. However, it is noted that the transmittance does not recover the initial value (100%) completely even after 3 days.

**Time-Resolved Light Scattering Measurements.** To confirm the SD type phase separation of the gel, we performed time-resolved light scattering measurements after a temperature jump from −40 to 25 °C. The measurements were done in a $Q$ range of $3.6 \times 10^{-4}$–$3.4 \times 10^{-3}$ Å$^{-1}$; it took 2.5 min for one $Q$-scan. The time evolution of the observed scattering intensities $I(Q)$ is shown in Figure 4a,b, where the time indicated represents the starting time of each measurement. Note that the scattering intensity $I(Q)$ at $t = 0$ was measured at −20 °C because the structural evolution at 25 °C is very fast compared with the $Q$-scanning time within the range of $3.6 \times 10^{-4}$ to $3.4 \times 10^{-3}$ Å$^{-1}$. The scattering intensity $I(Q)$ at $t = 0$ min thus obtained is almost $Q$-independent, showing no special structure in the observed $Q$ range. On the other hand, the intensity $I(Q)$ at 2.5 min shows a broad peak at around $1.6 \times 10^{-3}$ Å$^{-1}$, corresponding to a characteristic wavelength $\Lambda_m = 0.39$ $\mu$m, and $I(Q)$ increases with time without changing the peak position. These are the characteristic features of the SD type phase separation in the early stage. Here it should be noticed that this characteristic length ($\Lambda_m = 0.39$ $\mu$m) in the gel is smaller than that ($\Lambda_m = 0.6$ $\mu$m) for the fresh sample produced directly by quenching the homogeneous solution at 100 °C to 25 °C.[19] This is because the latter is considered to be the characteristic wavelength of SD for the solution before gelation while the former is for the gel network. As seen in Figure 4b, after 34 min the intensity curve $I(Q)$ hardly grows unless the gel was kept for a long time such as 1080 min; both the peak intensity and the position $Q_m$ almost remain constant. After a long time of 1080 min, however, the decrease of the intensity at around the peak position can clearly be noticed. In the spinodal decomposition of the usual fluids the peak position shifts toward lower $Q$ due to the domain growth. However, in the PVA gel the domain growth is hardly observed. Even if the volume shrinkage ($V/V_0 = 0.55$ at 500 min) of the gel is taken into account, the maximum domain growth is only 1.2 [$= \Lambda_m(500\ \text{min})/\Lambda_m(2.5\ \text{min})$]. This increase of the domain size is very small compared with SD in the usual liquids, suggesting that the domain growth is extremely suppressed.

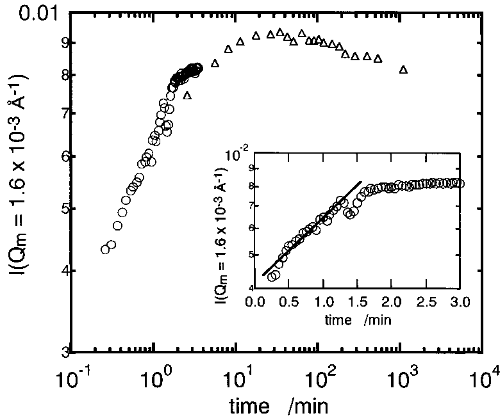

**Figure 5.** Time evolution of light scattering intensity $I(Q_m)$ at a peak position ($Q_m = 1.6 \times 10^{-3}$ Å$^{-1}$).

The growth rate of the scattering intensity $I(Q)$ is very fast in the early stage, especially in the first 2 min, so that we performed time-dependent measurements of the intensity at the peak position $Q_m = 1.6 \times 10^{-3}$ Å$^{-1}$ until 6 min without $Q$-scan. The observed time evolution of the intensity $I(Q)$ at $Q_m$ is shown in a log–log scale in Figure 5 where some $Q$-scan data are also included; the inset shows the semilog plot. The intensity increases very rapidly according to an exponential law in the very early stage until 1.5 min, suggesting again that the SD type phase separation occurs. After 1.5 min the growth rate is slowed down, but it still continues to grow and levels off at about 20 min. As mentioned in the Introduction, Onuki et al.[28] recently developed a Ginzburg–Landau model for gels undergoing SD decomposition under an assumption of fixed volume. This theory predicts the slowing down of the rate of domain growth observed here; the surface tension causing the driving force of domain growth is suppressed by the elastic force of the gel.

During the period between ~20 and ~200 min, both the UV transmittance and the scattering intensity at $Q_m$ are almost constant as seen in Figures 3b and 5, respectively, while the gel continues to shrink until 500 min (Figure 3a). After this volume equilibrium, the UV transmittance reversely increases and the scattering intensity $I(Q_m)$ decreases. The former recovers by about 5% of the minimum transmittance reached and the latter by about 10% of the maximum intensity attained. As mentioned in the previous section, the gel should become completely homogeneous by attaining another new volume equilibrium to relax the internal fluctuations brought about by the SD. Hence, the increase of the UV transmittance and the decrease of the scattering intensity must correspond to the relaxation process of the internal fluctuations. This structural relaxation may occur mainly in a range of the characteristic wavelength ($\Lambda_m = 0.39\ \mu$m) because the scattering intensity decreases at around the peak position $Q_m$ (see Figure 4b). Unfortunately, the present data are poor to discuss the kinetics of the relaxation in detail.

Here we have to pay our attention to the facts that the transmittance as well as the scattering intensity does not recover to the initial values at $t = 0$ min. This suggests that a part of the microscopic internal fluctuations produced by the SD is preserved even after the new volume equilibrium state, which contradicts the prediction of the theory. The reasons are not clear at the moment although some possibilities are considered. One is that it takes much longer time to attain the new *real* volume equilibrium state. Another possibility is that the internal fluctuations produced during the SD are frozen in by additional pinning points after the phase separation of the gel; for example, so-called dangling chains are incorporated with the cross-linking points (crystallites) in the shrunken phase during the SD process. This new cross-linking points would preserve or freeze the internal fluctuations.

## Conclusion

In this work, we have studied the phase separation of the transparent gel in the unstable region by UV transmittance, volume, and time-resolved light scattering measurements. It was found that the light scattering intensity $I(Q)$ has a peak at $Q_m = 1.6 \times 10^{-3}$ Å$^{-1}$, and the peak intensity $I(Q_m)$ increases exponentially with time without changing the position, suggesting that the SD type phase separation occurs in the gel. These changes finished within the first 2 min after the temperature jump without any appreciable volume change. After this early stage, in contrast to SD in usual fluids, the growth rate of $I(Q_m)$ is extremely slowed down, and the peak position does not change even after the early stage. This is the so-called pinning effect due to the elastic force of the gel predicted by the theory.[28] After the period of ~20 to ~200 min with constant scattering intensity, it began to decrease during the volume shrinking process, which must correspond to the relaxation process of the microscopic internal fluctuations produced by the SD. However, a part of the fluctuations could not be relaxed even after attaining the new volume equilibrium, contradicting the prediction of the theory.

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