

Rheological and structural studies on gelation of 12-Hydroxystearic Acid Solution

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Gelation for solutions of a low-molecular weight gelator, 12-hydroxystearic acid in organic solvents was investigated by using both rheological and X-ray scattering measurements. The gelation properties strongly depend upon kinds of solvents. The structures of the gels at different quench depths are essentially similar, although the magnitude of the elastic modulus and the scattering intensity depends upon them. The small-angle X-ray scattering studies reveal that the fibrillary network of the gel is denser at deeper quench.

Key words: gelation, low molecular weight gelator, rheology, X-ray scattering, sol-to-gel transition

1. INTRODUCTION

Recently, numerous studies have made on gelation of solutions of low molecular weight gelators in organic solvents [1]. This group of chemical compound has an ability to gel various kinds of organic solvents with a concentration of only a few percents due to formation of rigid fiber at nanoscales. Usually the gel is thermally reversible, i.e., gel is formed by cooling a mixture of gelator and solvent below the sol-to-gel transition temperature, while it transforms into sol by raising temperature.

Fatty acid derivatives such as 12-hydroxyoctadecanoic acid (HOA) or 12-hydroxystearic acid (HSA) are well-known as one of the low-molecular weight gelators [1-5]. It has been clarified in earlier studies that fibrillary or ribbonlike networks with rigid junction zones are formed in the gel. In the fibers, the hydroxy groups at C₁₂ are connected to the neighboring molecules by hydrogen bonding along the fiber axis [4,5]. So far, although the structures of the gel were largely investigated, there are few studies on dynamics of the gelling process such as quench depth dependence on the gelation. In this paper, we focus on the gel properties and the gelation process near the sol-to-gel transition temperature.

2. EXPERIMENT

2.1 Sample and sample preparation

HSA was purchased from Wako Chemical Co. and used without further purification. HSA with desired concentration was dissolved in organic solvents or phenyl methyl silicone (KF54, Shinetsu Chemical Co. Ltd.) by raising temperature. Afterwards, the sample was brought into a gel state by lowering temperature.

2.2 Viscoelastic measurement

We investigated rheological change during the gelation process by means of freely damping

oscillation technique (Rhesca Model RD-1100 AD coaxial cylinder-type torsional viscoelastometer). 4.5 ml of the solution was poured between outer cylinder (Pyrex tube with 13.9 mm i.d.) and inner cylinder (stainless rod covered with Pyrex tube with 8 mm o.d.) and set in an air bath in the apparatus. Rotating the inner cylinder up to the shear angle at 0.2°, a freely damping oscillation was induced by elastic restoring force of the sample and a piano wire supporting the inner cylinder.

2.3 X-ray scattering measurement

X-ray scattering measurements were conducted to investigate the structure of the HSA gel with an apparatus at the beam line BL-9C of High Energy Accelerator Research Organization in Tsukuba, Japan. The specimen for the scattering measurements were injected into a capillary tube made of quartz with a diameter of 1.5 mm. In some cases, we carried out time-resolved scattering experiments by using a temperature-jump cell designed for investigation of the structural development during the gelation process. The cell is composed of two blocks, where temperatures can be controlled separately, and we can make an instantaneous temperature-jump by moving the blocks up or down with a remote controller. In the time-resolved experiments, we pursued the structural development of the scattering intensity after temperature-jump from a sol-state (at higher temperature) into a gel-state (at lower temperature). The accumulation time of the measurements was 111 sec. The data were corrected for the empty cell and the transmittance.

Table I Solvent dependence of gel properties of HSA solution. THF: tetrahydrofuran, OG: opaque gel, TG: transparent gel, S: solution, I: insoluble.

dodecane	hexane	phenyl methyl silicone	toluene
OG	OG	OG	TG
xylene	ethanol	THF	water
TG	S	S	I

3. RESULTS and DISCUSSION

Firstly we investigated solvent effect on gelation of HSA solution. Observation was made at room temperature (ca. 25 °C) and for solutions with concentration of 3 wt % HSA. The result is summarized in Table I. As is clearly shown, HSA is soluble in solvents with polar groups such as ethanol or tetrahydrofuran, while HSA forms gel in hydrocarbon solvents. Especially, transparent gel was obtained for solvents with phenyl groups such as toluene and xylene, while turbid gel was obtained for usual hydrocarbon solvents such as hexane and dodecane. Thus, ability to form gel significantly depends upon solvent quality. In polar solvents, hydrogen bonding between HSA and the solvent or solvation is predicted to stabilize the solution. In the following experiments, we used toluene and phenylmethylsilicone (silicone oil) as typical solvents that yield transparent and turbid gels, respectively. The viscoelastic behavior strongly depends upon thermal history, e.g., the viscoelasticity in the cooling process is considerably different from that in the heating one (not shown). Therefore, in order to investigate sol-to-gel transition temperature T_g , we measured the time course of the viscoelastic behavior after quench from a temperature (ca. 70 °C, sol state) into given temperatures. Namely, if elastic modulus G or viscosity after quench into a given temperature increases more than that expected from the temperature dependence in the sol state, we assessed that the solution are in a gel region at this temperature. As shown in Figure 1, at low temperatures (until 66.2 °C), G increases with time after quench, while it does not change with time at temperatures higher than 66.6 °C. Thus, the transition temperature is expected to be in the range between 66.2 to 66.6 °C for the silicone oil solution with a concentration of 0.4 wt% HSA. Moreover, the deeper the quench, the larger the elastic modulus. We obtained the transition temperatures as a function of HSA concentration

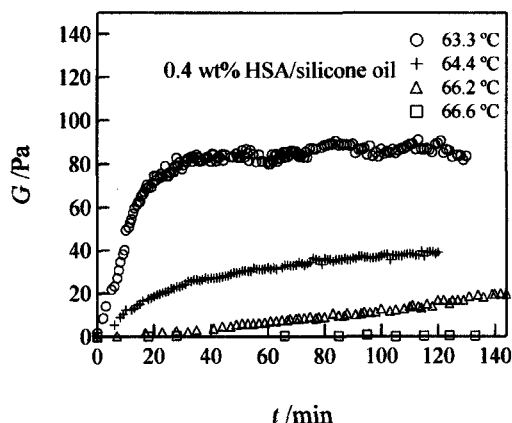


Fig. 1 Time course of elastic modulus after quench to the indicated temperatures for the solution with a concentration of 0.4 wt% HSA.

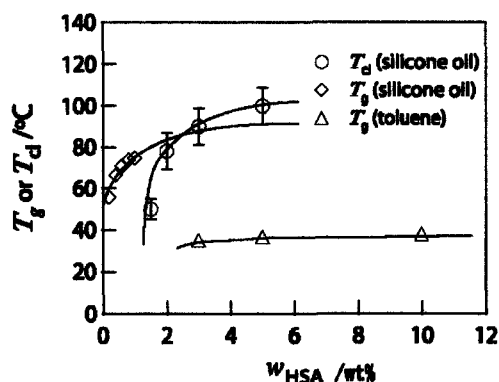


Fig. 2 Sol-to-gel transition temperature and cloud point curves for silicone oil gel (opaque gel) and toluene gel (transparent gel). Solid lines are drawn for visual guide. The error bars of sol-to-gel transition are within symbols.

by carrying out similar measurements for specimens with other concentrations. Furthermore, cloud points (temperatures) T_c were obtained by visual observation of the samples. These results are presented in Fig. 2. We also show the result of the sol-to-gel transition temperatures for the solution of HSA in toluene which forms the transparent gel. For the solution of HSA in silicone oil, which forms turbid gel, the sol-to-gel transition temperatures are shown to be higher than cloud points at low HSA concentration, while they can be lower at high HSA concentration. On the other hand, the transition temperatures of the HSA solutions in toluene are much lower than those in the silicone oil. This result suggests that the solution of HSA in toluene is more stabilized than that of

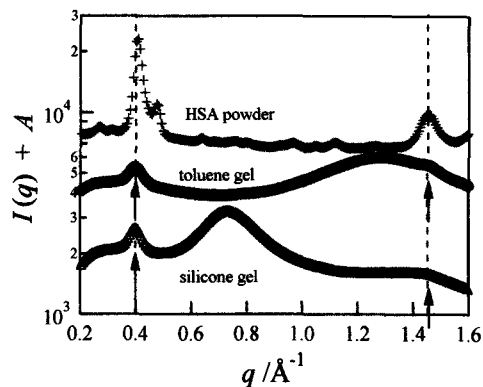


Fig. 3 Wide-angle X-ray scattering profiles for HSA crystalline powder, toluene gel (5 wt% HSA) and silicone oil gel (1 wt% HSA). A is a shift factor.

HSA in silicone oil. In Fig. 3, we show the wide-angle X-ray scattering profiles of the HSA crystalline powder, the gelled system in toluene and the gelled system in silicone oil at room temperature. The scattering intensity is shifted for clarity in the figure. The scattering profile for the HSA powder has a large peak and a small peak at $q = 0.41 \text{ \AA}^{-1}$ and 1.45 \AA^{-1} , respectively, as indicated by arrows, where q is the wavenumber defined by $(4\pi/\lambda)\sin(\theta/2)$. λ and θ are the wavelength of X-ray and the scattering angle, respectively. The former peak is attributed to (003) Bragg reflection of HSA crystalline established by Tachibana et al. [2,3]. The scattering profile for the gelled system in toluene and in the silicone oil has a peak and a shoulder at almost the same q as that for the HSA powder. The former peaks for both gels, however, slightly shift toward lower q and are broader than that for the HSA powder. Thus, it is shown that crystalline structure of HSA plays a significant role in the gelation.

We present the results of small-angle X-ray scattering measurements. Figure 4 shows quench depth dependence of the scattering profiles for the gelled system in toluene with a concentration of 10 wt % HSA. All the data were measured for the gel formed by quench from 49°C . There exists a scattering peak at $q = 0.13 \text{ \AA}^{-1}$, (001) reflection peak of HSA crystalline [2-5]. Moreover, the scattering profiles have a similar shape at different quench depths, suggesting that the structure of the gel is not essentially affected by quench depth. On the other hand, the deeper the quench depth, the larger the intensity. In the q -range from 0.04 to 0.065 \AA^{-1} , the scattering behavior obeys the Porod law [6], or the power law of -4 in the high q limit, reflecting a sharp interface of the fiber made of crystalline structure of HSA (Fig. 5):

$$I(q) \propto S q^{-4} \quad (1)$$

where S represents the total surface area of the crystalline structure. It is shown in Fig. 5 that the magnitude of $I(q)q^4$ is larger, as the quench depth is deeper, i.e., the total surface area of the structure is larger as shown in Eq. (1). This result implies that the fibrillary network is denser at deeper quench depth. This trend is also suggested from viscoelastic measurements for the gelled system in silicone oil as shown in Fig. 1, i.e., the elastic modulus is larger at deeper quench depth. Figure 6 presents the time development of the scattering profiles for the gelled system in toluene after quench from 49°C into 34.9°C . The scattering intensity increases with time t , reflecting formation of fibrillary

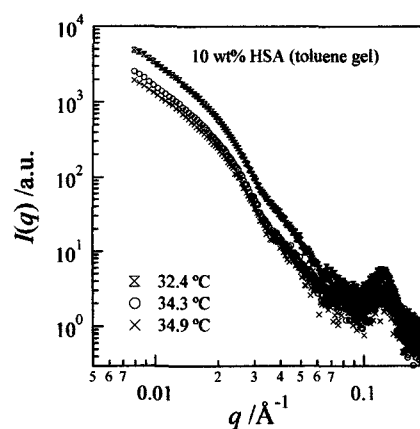


Fig. 4 Small-angle X-ray scattering profiles for the gelled system in toluene (10 wt% HSA) at different quench depths.

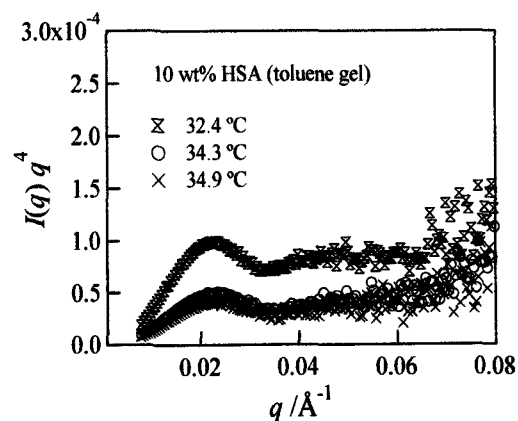


Fig. 5 Porod plot for gelled system in toluene with a concentration of 10 wt% HSA at different quench depths.

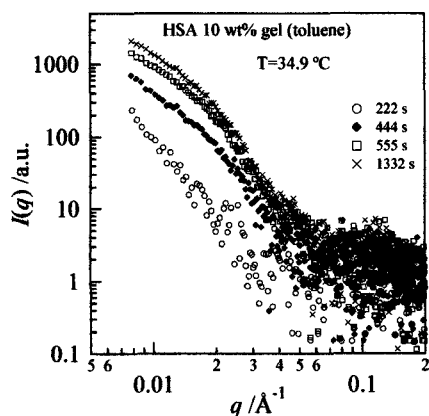


Fig. 6 Time development of scattering profiles at $T=34.9\text{ }^{\circ}\text{C}$ for gelled system in toluene quenched from $49\text{ }^{\circ}\text{C}$ (10wt %HSA).

network. The characteristic peak at $q = 0.13\text{ }\text{\AA}^{-1}$ is not clear for short accumulation time of the measurements. After ca. $t = 444\text{ sec}$, the shape of the scattering profiles is similar, although the scattering intensity still continues to increase with t . Thus, it is shown that fibrillary structures develop with self-similarity.

CONCLUSION

We investigated the gelling process of 12-HSA in organic solvent by means of rheological and scattering techniques. The properties of gelation significantly depend upon solvent quality. Structures of the gel are essentially unchanged irrespective of quench depth. Fibrillary structures develop with self-similarity.

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References and Notes

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