Self-assembling Structures and Sol-Gel Transition of 12-Hydroxystearic Acids in Organic Solvents

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Introduction

In recent years a large number of studies have been made on the gelation of low-molecular weight molecules in organic solvents [1]. The organogels exhibit thermally reversible sol-gel transition and the gelators spontaneously aggregate into fibers below the gelation temperature peculiar to the system. The fibers form three-dimensional network structures in the organic solvents, so that the solution is solidified.

12-Hydroxystearic acid (12-HSA) is well-known as one of low-molecular weight gelators. In this study we investigate structures and gelation properties of three types of 12-HSA gels using different kinds of solvents, (i) transparent gel, (ii) turbid gel (iii) gel transformed from turbid gel into transparent gel or vice versa, by changing the concentrations or temperatures. The X-ray scattering experiments were carried out at two sample-to-detector distances of 2260 mm (small-angle X-ray scattering) and 524 mm (wide-angle X-ray scattering).

Results and Discussion

Figure 1 shows wide-angle X-ray scattering profiles of 12-HSA powder and 7 wt% 12-HSA gels in polybutadine (PB) oligomer, dodecane and toluene. The scattering profiles of the powder and the gels have two large peaks at q = 0.13 Å⁻¹ and 0.41 Å⁻¹. These peaks (dashed lines) were attributed to (001) and (003) Bragg reflections, respectively, by other researchers [2]. Thus, the self-assembling structures of the gels are considered to be composed of crystalline structures of 12-HSA. When we take a careful look at the X-ray scattering profiles in Figure 1, the scattering peak of the gel in toluene slightly shifts toward smaller q and is broader in comparison with those of other gels. The latter result suggests that the crystalline size of the gel in toluene is smaller than those of other gels.

The form factor P(q) from the rod particles with length *L* is described by

$$P(q) = \frac{L\pi}{q} I_c(q) \tag{1}$$

for $2\pi / L << q$ where $I_c(q)$ is related to the scattering intensity from the structure of the particle in the cross section. For $2\pi / L << q << 2\pi / R_c$, $I_c(q)$ can be represented by the Guinier-type scattering behaviour,

$$I_c(q) = A^2 \exp\left(-\frac{R_c^2 q^2}{2}\right)$$
(2)

where A and R_c are the area of the cross-section and the radius of gyration of the cross-section of fibers, respectively. Thus, linear relation between $\ln(Iq)$ vs q^2 is obtained from eqs. (1) and (2). We show a plot of $\ln(Iq)$ vs q^2 obtained from SAXS measurements for 12-HSA gels in toluene (transparent gel) in Figure 2. We estimated the value of R_c from the slope of the figure. As a result, the value of R_c had almost the same values (82 - 85 Å) for gels with various 12-HSA concentrations and was not almost affected by the HSA concentration. The further SAXS analysis reveals that the cross-section of fibers has square or circular shape (no anisotropic shape) [3].



Figure 1 Wide-angle X-ray scattering profiles of 12-HSA powder and the 7 wt% 12-HSA gels in PB oligomer, toluene and dodecane.



Figure 2 Plot of ln(Iq) vs q^2 for 12-HSA gel in toluene.

References

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