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Gelation Process of Organogels Investigated by Time-Resolved Small-Angle X-ray Scattering Techniques

*Hiroyuki TAKENO, Tomomitsu MOCHIZUKI and Atsushi TAKEI
Department of Chemistry and Chemical Biology, Faculty of Engineering, Gunma University,
Kiryu, Gunma 376-8515, Japan

Introduction

Some low molecular weight materials can gelate organic solvents at very low concentrations. The materials are called low-molecular weight gelators. They form a three-dimensional network of crystalline fibers in an organic solvent and cause gelation [1]. The phase behaviour of the sol-gel transition in the gelator/solvent systems depends on the melting behavior of the crystallites, and the sol-gel transitions exhibit thermally reversible behaviour. Though numerous studies have so far been conducted on structures of the gels, to our knowledge, few studies have been made on the structural development during the gelation process. This is because the structural evolution is usually so fast and therefore it is difficult to experimentally pursue it. Synchrotron X-ray scattering measurements are a very powerful technique to investigate such fast structural evolution.

In this study, we investigated the structural evolution during the gelation process for a mixture of 12-hydroxystearic acid (12-HSA) / an organic solvent by using time-resolved synchrotron small-angle X-ray scattering technique.

Experimental Section

12-HSA (purity 99%) was purchased from Aldrich Co. and used as received. After 12-HSA with a known concentration was dissolved in a solvent by raising temperature, it was cooled at room temperature in order to prepare a gel. Time-resolved small-angle X-ray scattering measurements were performed at the beam line 15A by using a temperature-jump cell. The SAXS data were taken at various times, after the sample was quenched from a sol state into a gel state. The scattered intensity was detected with an image intensifier coupled to a CCD camera. The two dimensional scattered images were circularly averaged to obtain the scattering profiles as a function of the scattering vector q defined by $q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle. The background scattering intensity was subtracted from the scattering intensity of the sample. The subtracted data were normalized by the intensity of the incident beam and the exposure time of the measurement.

Results and Discussion

Figure 1 shows time-evolution of scattering profiles for 10 wt % 12-HSA gel in xylene after temperature-jump from 55 ℃ (sol state) into 36 ℃ (gel state). At the early stage ($t \leq 27$ sec), the scattering profiles did not change with time. This stage corresponds to induction period. Afterward, the scattering intensity increased with elapse of time, while any scattering peak did not appear in the q-range covered in this study at $t \leq 31$ sec. At the next stage ($t > 31$ sec), a scattering peak appeared at $q = 0.13$ Å^{-1}. According to the previous study, this peak corresponds to (001) reflection [2]. The scattering intensity in the small q range also became larger with time. The scattering behavior in the small q-range can be represented by the form factor of rod particles. Thus, our result suggests that the crystalline fibers were formed and grew. In summary, the gelation process can be divided into three stages. After induction period (stage I), the concentration fluctuations increased but the Bragg peak did not appear in this stage (stage II). In stage III, nucleation took place at $t \cong 31$ sec and afterward the crystalline fibers grew. During the growth of the fibers, the shape of the profiles did not almost change. This result indicates that the fibers grew with keeping the cross-sectional size almost constant.
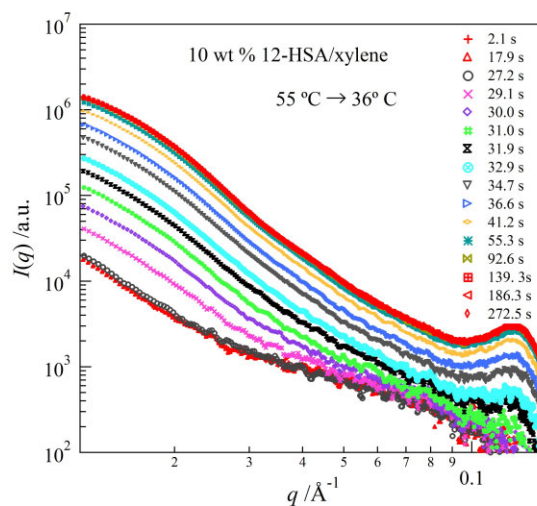

Figure 1 The scattering profiles for 10wt % 12-HSA gel in xylene at various times during the gelation process.

References

[1] P. Terech, R.G. Weiss, Chem. Rev. 97, 3133 (1997).
[2] H. Takeno, T. Mochizuki, K. Yoshiba, S. Kondo, T. Dobashi, Prog. Colloid Poly. Sci. 136, 47 (2009).

* takeno@gunma-u.ac.jp