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Structural Studies of 12-Hydroxystearic Acid Gels in Ionic Liquid

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1 Introduction

Low-molecular weight gelator forms a self-assembled fibrous network in various kinds of solvents. The network is usually formed through physical interactions such as hydrogen bonding, ionic interactions, π-π interactions, van der Waals interactions etc. and the sol-gel transition is thermally reversible.

12-hydroxysteric acids (12-HSA) is well-known as one of organogelators. 12-HSA gelates in some ionic liquids as well as organic solvents. Due to excellent properties of ionic liquids such as thermal stability, nonflammability, negligible volatility and high ionic conductivity, gels using ionic liquids as a solvent has potential applications in electrochemical field such as batteries as solid state electrolyte. 12-HSA forms crystalline fibers in various solvents, and gelation is caused by three-dimensional network of the crystalline fibers. It has recently been reported that 12-HSA has different polymorphs [1, 2], depending upon kinds of solvent and temperature. It has been shown in the previous study that the polymorphs affect the morphology of the self-assembled structures.

In this study, we investigated structures and ionic conductivity of 12-HSA gels in ionic liquids prepared by various thermal history.

2 Experiment

In this study we used 12-HSA as a gelator and 1-Allyl-3-butylimidazolium Bis (trifluoromethanesulfonyl) imide [ABIm] [TFSI] as a solvent. Simultaneous synchrotron small-angle and wide-angle X-ray scattering (SAXS / WAXS) measurements were performed at the beam line 6A and 10C. The scattered intensity was detected with PILATUS. The two dimensional images were circularly averaged to obtain the scattering profiles as a function of the scattering vector q defined by $q = 4\pi \sin(\theta/2)/\lambda$. Here θ and λ are the scattering angle and the wavelength of X-ray, respectively. The scattering data were corrected for the background scattering, the intensity of the incident beam and transmission. The ionic conductivity for 12-HSA/[ABIm][TFSI] gel and [ABIm][TFSI] was measured using an electrochemical apparatus with a frequency response analyzer (Solartron 1280Z) in the temperature range from sol state to gel state.

3 Results and Discussion

Fig. 1 shows scattering profiles of 3 wt % 12-HSA/[ABIm][TFSI] gel prepared by temperature-jump from a sol state into a gel state. At a low temperature (34 ºC) the profile had a broad peak at q = 0.136 Å^{-1}, which corresponds to the (001) peak, whereas at 60 ºC three peaks were observed at q = 0.136, 0.147, 0.159 Å^{-1}. These different (001) peaks were also observed for neat 12-HSA, suggesting that 12-HSA has at least three different polymorphs. When temperature is increased, the peak at q = 0.147 Å^{-1} was developed (75 ºC). Thus, stability of each polymorph is affected by temperature variation.

We carried out electrochemical measurements for 12-HSA/[ABIm][TFSI] gel and [ABIm][TFSI] and obtained ionic conductivity as a function of temperature. Temperature dependence of the ionic conductivity obeyed the Arrhenius equation for both 12-HSA/[ABIm][TFSI] gel and [ABIm][TFSI] (not shown here). The ionic conductivity of 12-HSA/[ABIm][TFSI] gel was almost the same as that of [ABIm][TFSI]. This result indicates that the self-assembling structures in the gel or different polymorphs do not affect the ionic conductivity.

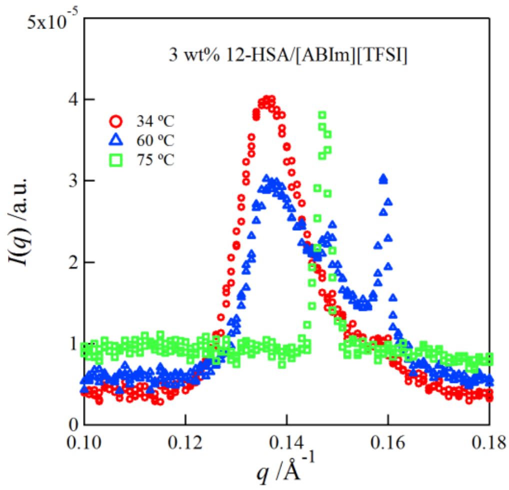

Fig. 1 Scattering profiles of 3 wt% 12-HSA/[ABIm][TFSI] gel prepared by temperature-jump from a sol state into a gel state at various temperatures.

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References

[1] H. Takeno, M. Yanagita, Y. Motegi, S. Kondo, *Colloid. Polym. Sci.*, **293**, 199 (2015).
[2] S. Wu, J. Gao, T.J. Emge, M.A. Rogers, *Crystal Growth & Design*, **13**, 1360 (2013).

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