Thermal transition of viscoelasticity and association structure of small molecule gelator with metal ions

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1. Introduction

It is known that some groups of small molecules associate with each other to form a large size of aggregate in solution state. Such solutions show some specific viscoelasticities such as gelation and large viscosity. Among such small molecules, small molecule galator containing metal ions is one of major interesting groups. We investigated such small molecule gelator and found that some of them showed thermal transition on viscoelstic properties, such as complexes of alkyl triazine and platinum or copper and so on. We preliminary found some of the small molecule gelators with metals showed a heat-set type of thermal gel-transition. In this study, we investigated thermal transition of viscoelsticity and association structure of such small molecule gelators containing metal ions.

2. Rheological properties of the samples

We prepared complexes of alkyl triazine and metals such as platinum and copper with the molar ratio of 3:1 in tetrachlorocarbon, chloroform and dichloromethane. These complexes showed highly viscous property at room temperature. When the solution of platinum complex was heated to 50oC, the viscous solutions changed into gels even when their concentration was below 1wt%. Dynamic viscoelstic measurements on these solutions showed that, at higher temperature, the storage modulus G ’was almost independent of angular frequency and almost one order higher than loss moduls G ”, which confirmed that the sample was gel in this state. On the other hand, at lower temperature regions, G ”became higher than G ” for low angular frequency regions. Creep and creep recovery measurement confirmed flow property of the samples. The thermal transition was found to occur between 30oC and 50oC. Furthermore, the transition was found to be reversible.

3. SANS meaturements

SANS measurements were carried out by SANS-U spectrometer at the Neutron Scattering Laboratory of the ISSP, The University of Tokyo, established at C1-2 beam line of JRR3M in JAERI (Tokai), Ibaraki, Japan. The wave length and beam size of incident neutrons was 0.7 nm and 3mm, respectively. The temperature was 25oC. Tetrachloromethane and deutrated chloroform, dichloroethane and decaline were used as solvents.

The atom of chlorine is know to have large absorption property of neutron. The solvents used in this study contained chlorine atoms, so that it needed to spend long time to carry out scattering measurements. For tetrachloromethane solutions, we must have spent more than ten hours on one shot measurements and could not have enough high contrast data to analyze the scattering profile to manifest the structure after substruction of background scattering. As for deutrated dichloroethane, we can meatured scattering profile by several hours measurement for one shot. However, as well known, its boiling point is not high enough to analyze the thermal transition of the gels at high temperature exceeding 50oC. In this study, we found that deuterated chloroform can be used to measure for the thermal transition of association structure when we spend at least several hours on one shot measurement. From the measurement of the deuterated chloroform sample, the gelator formed one dimensional aggregate with diameter around 3nm at room temperature. In this study, we could not measure at the other temperatures. However, it is found that further measurements must manifest details of the

thermal structural change of the metal containing small molecule gelator.