

SANS Study on Structure of Critical Gelation Clusters

Xiang Li, Kazu Hirose

Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.

Tel: +81- 4-71363419, E-mail: x.li@issp.u-tokyo.ac.jp

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Introduction

At the sol-gel transition point, a viscous liquid changes into an elastic solid, and power law behaviors are observed in the static or dynamic properties. [1] The process of forming network has attracted much interest from many researchers to understand several scientific phenomena in modern statistical physics. Many theoretical studies have been performed to investigate the growing process of the gelation clusters against the reaction conversion, i.e. the bethe-lattice theory developed by Flory and Stockmayer and the percolation theory including the site and bond percolation processes. To examine the theoretical predictions, experimental studies also have been performed by means of the viscoelastic measurements, light scattering measurements etc. However, precise measurements of the reaction conversion and accurate reaction termination near the sol/gel transition point were extremely difficult because of uncertainty in the experiments. [2]

Recently, Sakai et al developed a novel polymer network called Tetra-PEG gel, [3] which is formed by AB-type cross-end coupling of two tetra-arm poly(ethylene glycol) (Tetra-PEG) units that have mutually reactive amine ($-NH_2$) and activated ester ($-OSu$) terminal groups, respectively. In our previous studies, we successfully measured the reaction conversion using the infrared spectroscopy. The reaction conversions of the end groups in Tetra-PEG gels were approximately 95% regardless of the ratio of Tetra-PEG prepolymers (Tetra-PEG- NH_2 and Tetra-PEG- OSu). Furthermore, the gelation occurs at low polymer concentrations of about 1 wt% in this method because of the high efficiency of the reaction between the amino and activated ester groups. With this gel, we precisely control the reaction conversion, the polymer concentration, and the ratio of units. With these parameters, we can examine three different critical conditions: the reaction-limited, the concentration-limited, and the unit ratio limited critical conditions. In this presentation, we report the results of the latter two conditions.

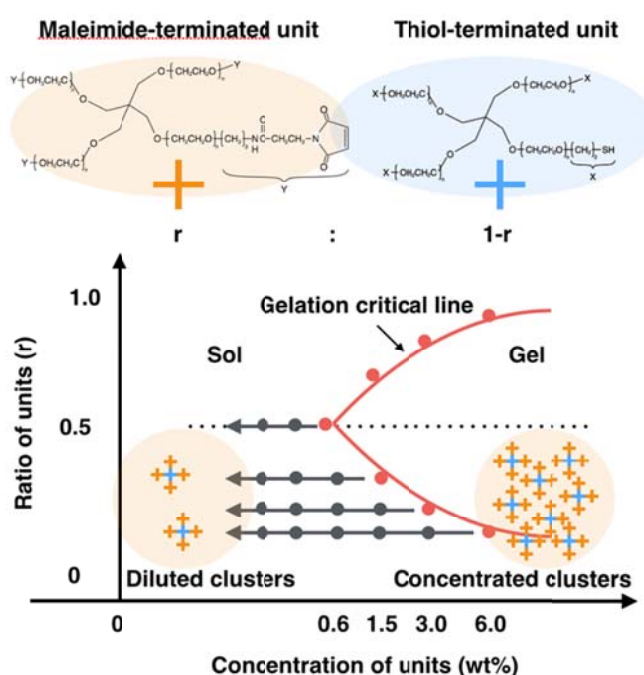


Figure 1. A schematic representation of phase diagram of sol/gel transition and preparation of critical clusters in Tetra-PEG system.

Experiments

Maleimide-terminated tetra-PEG (Mw 10k, PDI < 1.1) and thiol-terminated tetra-PEG (Mw 10k, PDI < 1.1) were dissolved in a 50 mM citric phosphate D₂O buffer (pH3.0) at various molar ratios and concentrations to form critical clusters right below the gelation point following the sol/gel phase diagram obtained in the previous study [4] (Figure 1). Small angle neutron scattering (SANS) measurements were performed by the SANS instruments QUOKKA in Australian Nuclear Science and Technology Organisation (ANSTO). Three different camera lengths 20, 8, 1.3m were used to obtain the scattering profiles in the q range of 0.003-0.7 Å⁻¹. All measurements were carried out at 25°C. The incoherent scattering was subtracted from all data with the values of $I(q)$ at $q = 0.7$ Å⁻¹ where coherent scattering was negligible.

Results and discussion

Scattering profiles of the concentration-limited critical clusters and their dilutions were shown in Figure 2. All of the $I(q)$ obeyed the relationship $I(q) \sim q^{-2}$ which is predicted by both bethe-lattice theory and the simulation of percolation theory. The shoulder around $q = 0.005$ Å⁻¹ may represent the largest clusters in the system. Scattering profiles of the molar ratio-limited critical clusters were shown in Figure 3. A clear shoulder around $q = 0.1$ Å⁻¹ was observed for the sample with 6wt%. As the 6wt% is just above the overlapping concentration of the tetra-polymers, the shoulder may represent thermal fluctuations of the packed cluster's polymers. Unlike the results of the concentration limited condition, the diluted clusters (6 to 0.1875 wt%) obeyed a different power relationship $I(q) \sim q^{-1.6}$.

References

- [1] M. Rubinstein and R. H. Colby, Polymer Physics, *Oxford University Press*, 2003
- [2] J. P. Cohen Addad, Physical Properties of Polymeric Gels, *Wiley*, 1996
- [3] T. Sakai et al., *Macromolecules*, 41, 5379–5384, 2008
- [4] T. Sakai et al., *Polymer Journal*, 2016 (In press)

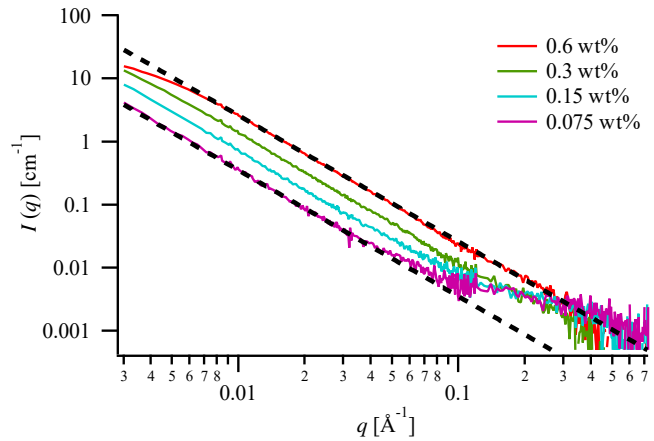


Figure 2. Scattering profiles of concentration-limited critical clusters near gelation point and its dilution. The dotted lines show the guide lines of $I(q) \sim q^{-2.0}$.

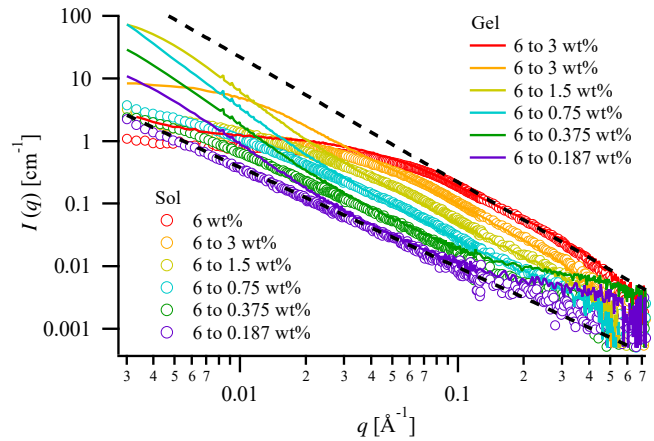


Figure3. Scattering profiles of the molar ratio-limited critical clusters near gelation point and its dilution were shown as empty circles, and scattering profiles of the gels made by these clusters were also shown in this figure as solid line. Broken lines show the guide lines of $I(q) \sim q^{-2.0}$ and $I(q) \sim q^{-1.6}$, respectively.