論文の内容の要旨

Dynamic and Static Structural Analysis of Model Polymer Network Gel under Deformation

（モデルネットワークゲルの変形時における動的及び静的構造解析についての研究）

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Polymer gels are ubiquitous materials in our daily life. A typical example is foods such as jelly and boiled eggs. The organisms are also gels. The synthesized polymer gels are widely used for medical applications. For example, contact lenses, super absorbers of diapers, and so on. These applications utilize the solvent retention ability of gels, which is one of the unique features of gels. The existence of solvent also enables gels to accommodate small molecules inside and sift them based on the size of molecules. Other than these, with the aid of various characteristic features of gels, gels are expected for applications to alternative biological tissue, carriers of drug delivery systems, soft electric devices, and so on.

However, understanding gels' physical properties have been challenging for a long time. One of the reasons is the heterogeneity of gels. The structure of gels usually contains various types of heterogeneities. For example, polymer strands and cross-linkers are often randomly distributed (spatial heterogeneity). Other types of heterogeneities are bond defects, such as loop structures, entanglements of the polymer strands, and so on (topological heterogeneities). These heterogeneities not only make the theoretical treatment of gel complicated but also degrade the physical properties of gels, such as mechanical strength and deformability. Since the gel structure is a huge system and heterogeneity is incorporated randomly, it is difficult to treat the effect of heterogeneity for these properties in theories and even computer simulations in a realistic time range. Therefore, increasing the homogeneity of gels contributes to both improving mechanical properties and understanding gel physics.

Recently, our research group succeeded in removing the spatial heterogeneity from the gels. Spatial heterogeneity had been thought of as an inherent property of polymer gels because the cross-linking "freezes"

the network structure. However, this preconception was broken from our simple and universal concept for the synthesis of gels. The homogeneous gel was fabricated based on a theoretical gelation framework “bond percolation”. There are three requirements in this hypothesis; the first is to use the prepolymers which have a high excluded volume effect, i.e., star polymers (prepolymer condition). The second is to use good affinity solvents for the prepolymers (solvent condition). The last is to prepare gels at a concentration above the overlapping concentration c* of prepolymers (concentration condition). The gels prepared in these conditions resulted in gels with high spatial homogeneity, even in a length scale of the wavelength of visible light, which is extremely higher than the scale of spatial heterogeneity of common gels.

My doctoral dissertation focuses on the structural analysis of model network gels, especially for the structures under deformation, using various scattering techniques, including light, X-ray, and neutron.

The first topic is understanding the criteria for the model network formation. Polymer gels are usually spatial heterogeneous. The heterogeneity is incorporated randomly into the gel network with the cross-linking reaction. Hence, the control of the heterogeneity is difficult. In this study, I broke the requirements to realize the bond percolation condition intentionally and introduced the different types of spatial heterogeneity into the gel network independently; the aggregation and the nano-voids (**Figure 1**). The static and dynamic structure was quantified with various scattering methods, and the validity of the bond percolation concept as the simple and universal concept was confirmed. These results suggest that we can fabricate the spatial homogeneous gel with a well-defined network structure regardless of polymer species. In the following, I focused on the structural analysis model network gel synthesized based on the bond percolation concept.

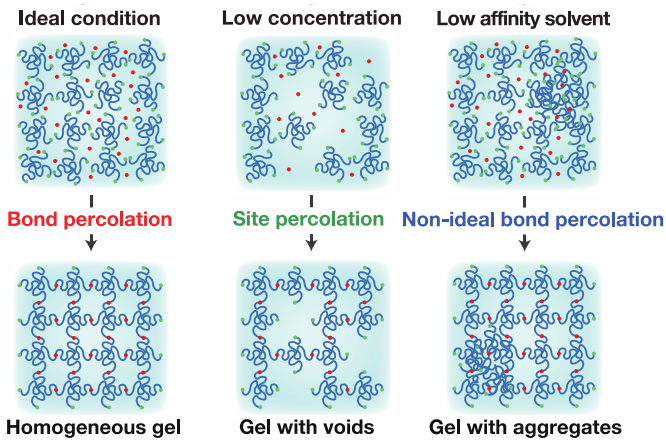

Figure 1. The schematic illustration for introducing the heterogeneities into a gel network. (left) spatial homogeneous gel, (central) gel incorporated with nano-voids, (right) gel incorporated with aggregations.

The second and third topics are about the static structure of the model network gels under deformation, i.e., uniaxial elongation and uniaxial compression. In these sections, the structural analysis was conducted with small-angle neutron and X-ray scattering. In the previous studies, the spatial heterogeneous structure not only degrades the physical properties of gels such as mechanical strength and deformability but also disturbs the structural analysis with scattering methods due to the strong contribution of spatial heterogeneity in the scattering intensity. In these sections, I first showed the effectiveness of the removal of spatial heterogeneity for the improvement of the mechanical properties of gels. The spatial homogeneity also contributed to clarifying the structural features in the wide-scale range where the structure has been obscured

so far due to the spatial heterogeneity. From the scattering result, the quantitative information could be extracted with model fitting, which contributed to the understanding of the deformation mechanism of gels.

The final topic is the dynamic structural analysis of the model network gel under compression with the quasi-elastic neutron scattering (QENS). Using the deuterium labeling and neutron scattering, I extracted the dynamics of the particular part of the network. The structure of compressed gel is anisotropic. In QENS experiment, it is possible to obtain the dynamics for each direction independently depending on which direction we detect the scattered neutron. The experimental result revealed the orientation dependence of the dynamics. This might be due to the variation of the solvation structure with compression; however, it is not clear currently. Further investigation should be conducted.

In this doctoral dissertation, I first established the synthesis strategy of the model network gels based on the simple and the non-constrained by polymer species concept. Spatial heterogeneity had been a long-standing problem in gel science, which hinders the understanding of the structural property of gels. I proposed the solution for this problem in this dissertation and demonstrated the utility of such gels for structural analysis with scattering methods. I conducted the structural analysis for spatial homogeneous model network gels in various aspects, and the results contributed to the understanding of the universal properties of gels under deformation through structural analysis with scattering methods.