<div align="center">論文の内容の要旨</div>

論文題目　Structural analysis of polymer aggregation induced by hydrophilic and hydrophobic interaction

<div align="center">（親水性・疎水性相互作用に起因する高分子の凝集構造についての研究）</div>

氏　　　名　　廣井　卓思

I. Introduction

　　Polymers are the molecules consisting of a small unit called "monomer". When these polymers are connected with each other, a macroscopic polymer network is formed. When this polymer network is immersed into appropriate solvent, a gel, i.e., a polymer network containing large amount of solvent, is prepared. Gels are widely used in our daily life and therefore indispensable materials. For applications of gel materials, a fatal problem is that conventional gels are brittle. To solve this drawback, various kinds of tough gels have been developed in recent years. Among of them, a gel called Tetra-PEG gel is focused in this thesis. Tetra-PEG gels are prepared by crosslinking of two tetra-arm polyethylene glycol (PEG) with different functional groups at the ends (Figure 1). Many experimental results strongly suggest that this preparation scheme introduces less inhomogeneities from the viewpoint of static structure. The first topic of this thesis is the elucidation of the inhomogeneities of the gels from the viewpoint of dynamics.
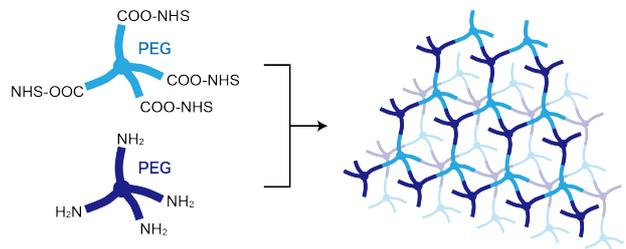

Figure 1. Preparation scheme of Tetra-PEG gel.

　　To measure inhomogeneities of gels by using light as a probe, an apparatus called dynamic light scattering microscope was developed. This apparatus can also measure the size distribution of opaque dispersion such as milk, ink and so on without dilution. Taking advantage of this unique feature, a structural analysis of opaque systems was performed and this is the second topic of this thesis. As representative opaque systems, carbon nanotube dispersions and heat-induced protein gels were investigated. Here, carbon nanotubes are regarded as representative hydrophobic materials and proteins are regarded as representative hydrophilic materials. Therefore, the structural analysis of these two extreme cases will show the comprehensive view of hydrophilic and hydrophobic interaction.

　　The final topic is the integration of the first topic and second topic; structural analysis of inhomogeneity-free amphiphilic gels. By replacing amine-terminated tetra-arm PEG with amine-terminated polydimethylsiloxane (PDMS), an inhomogeneity-free PEG-PDMS gel was successfully prepared. One of the interesting points of this system is that PEG is hydrophilic, while PDMS is hydrophobic. Therefore, the resultant gel shows microphase-separated structure when the solvent is water. In addition, this microphase-separated structure was controlled by varying the molecular weight of PDMS units.

II. Investigation of Inhomogeneities of Gels from the Viewpoint of Dynamics

II-1. Observation of multiscale dynamics by the combination of dynamic light scattering and neutron spin echo spectroscopy

Dynamics of Tetra-PEG gels was investigated by quasi-elastic scattering techniques. To see the dynamics in nanometer scale, the wavelength of source should be several nanometers. To achieve this microscopic measurement, cold neutron beam was used as a probe. Among the neutron quasi-elastic scattering techniques, neutron spin echo spectroscopy (NSE) can achieve the highest energy resolution (less than 1 μeV). By applying NSE to the Tetra-PEG gels, two interesting features were clarified. First one is that the relaxation mode is described as a solution-like mode (Zimm mode) in the spatial range less than 10 nm. This result indicates that Tetra-PEG gels are free from connectivity inhomogeneity (Figure 2(a)) and entanglements (Figure 2(b)). Through the combination analysis of quasi-elastic light scattering (dynamic light scattering; DLS) and quasi-elastic neutron scattering, quantitative analysis of the mesh size of Tetra-PEG was also performed (Figure 2(c)). Second interesting feature is that the relaxation occurs completely even in nanometer scale. This result indicates that Tetra-PEG gels have no frozen component. Like this, inhomogeneity-free nature of Tetra-PEG gels was proved from the viewpoint of dynamics.
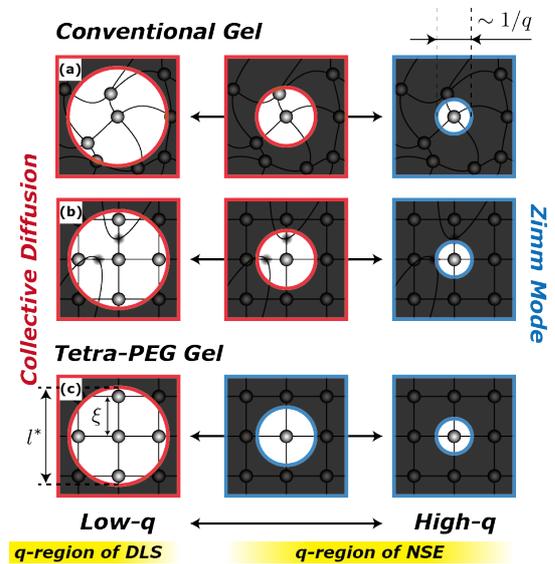

Figure 2. Comparison of gel dynamics.
(a) Gel with connectivity inhomogeneity.
(b) Gel with entanglement.
(c) Inhomogeneity-free Tetra-PEG gel.

II-2. Dynamic light scattering microscope

Although Tetra-PEG gel is almost inhomogeneity-free, there still remain small inhomogeneities in larger scale. This point was clarified from slight upturn in low-q region in small-angle neutron scattering (SANS) profiles. To measure these inhomogeneities in larger scale, DLS is one of the most promising tools. The scale of inhomogeneities of Tetra-PEG is estimated to be several μm. However, spatial resolution of conventional DLS system is around 100 μm. Therefore, conventional DLS system tells us only the spatial-averaged information. To achieve DLS with high spatial resolution, I developed an apparatus named dynamic light scattering microscope. It was clarified that

Figure 3. Concentration dependence of the size distribution of (a) polystyrene latex suspension and (b) Chinese ink.

DLS microscope has another interesting characteristic; it enables us to measure the size distribution of opaque dispersion. For examples, DLS microscope can measure the dynamics of thermo-responsive polymer gels as a function of temperature. To prove this, a measurement of the dynamics of representative thermo-responsive polymer, poly(N-isopropylacrylamide), was performed below and above lower critical solution temperature. As another example, concentration dependence of size distributions of polystyrene latex suspension (Figure 3(a)) and Chinese ink (Figure
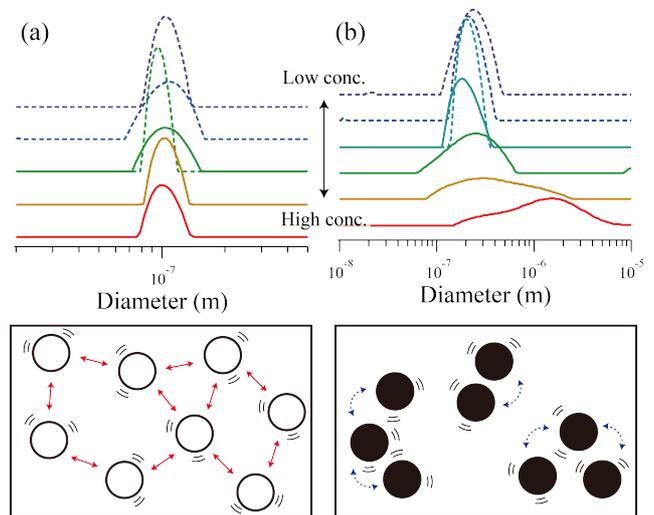
3(b)) was investigated in a wide concentration range from their dynamics. Here, polystyrene latex suspension is a representative of multiple scattering media, and Chinese ink is a representative of strong light absorption media. In the case of polystyrene latex suspension, there was no concentration dependence thanks to their surface charge. In contrast to this, a sign of collective motion was observed in the case of Chinese ink.

III. Aggregation induced by hydrophobic and hydrophilic interaction

III-1. Hydrophobic interaction: Carbon nanotube

DLS microscope enables us to perform structural analysis of opaque system governed by hydrophilic and hydrophobic interaction. As a representative system, concentration dependence of dispersion states of carbon nanotube (CNT) suspension was investigated. Since CNT strongly absorbs light, DLS measurement was available only for very dilute dispersion. Therefore, there was no report about the concentration dependence of the dispersion state of CNT suspension. However, the dispersion state in concentrated suspension is more important from the viewpoint of application. Measurement by DLS microscope revealed that there is dispersion-state transition at higher concentration region. In the case of extremely long CNT (super growth CNT), large aggregates were observed at the concentration higher than 0.3 wt% (Figure 4(a)). Note that the absorbance of the highest concentration is approximately 300 in 1 cm cell, which is impossible to access by conventional DLS systems. In addition, polarized DLS technique was also examined. By comparing the decay of time correlation functions of scattered light intensity obtained from polarized and depolarized configurations, the information of rotational Brownian motion can be obtained. Through the combination of DLS microscope and polarized DLS technique, it was revealed that the rotational motion is restricted at higher concentration region (Figure 4(b)).
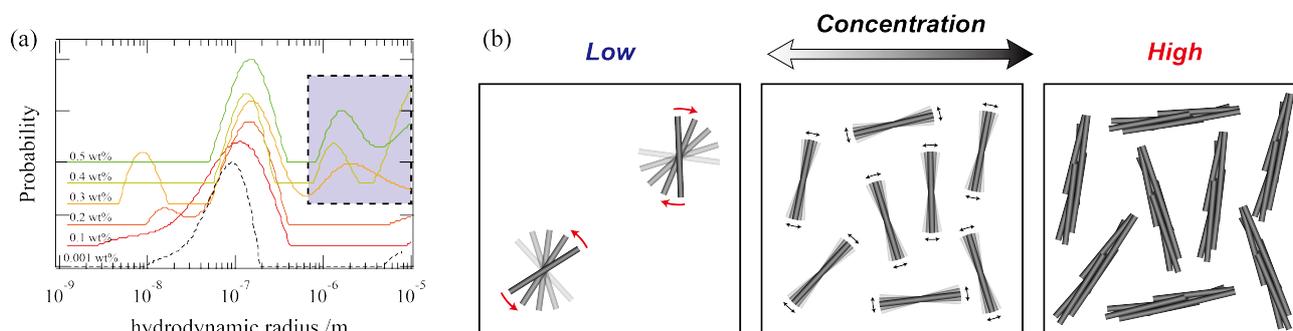

Figure 4. (a) Concentration dependence of the size distribution of super growth CNT suspensions.

(b) Proposed concentration dependence for aggregation state of CNT suspensions.

III-2. Hydrophilic interaction: Ovalbumin

As a representative hydrophilic system, ovalbumin (OVA), a major protein in egg white, was investigated. It is well known that OVA aggregates at high temperature. In salt-free environment, these aggregates are rod-like shape, similar to CNT. When the concentration of OVA solution is high enough, heated solution makes a gel. Although OVA is hydrophilic, it was revealed recently that hydrophlicity can be tuned by peptide treatment; OVA without 22 N-terminal residues, called pOVA, showed clear difference from intact OVA. The heat-induced gels prepared from OVA and pOVA are different in their turbidity and rheological properties. To investigate the origin of these macroscopic differences, structural analysis was performed by DLS and SANS. For OVA, SANS profiles obtained from

heated samples show clear peak structure whose peak position does not depend on the preparation concentration (Figure 5(a)). This result indicates that the aggregation growth induced by heating proceeds homogeneously. In contrast to this, SANS profiles of heated pOVA solutions do not show peak structure but show strong upturn originated from glass-like inhomogeneities (Figure 5(b)). This clear difference is explained by the existence of large aggregates in pOVA solution before heating, induced by their relatively high hydrophobicity.
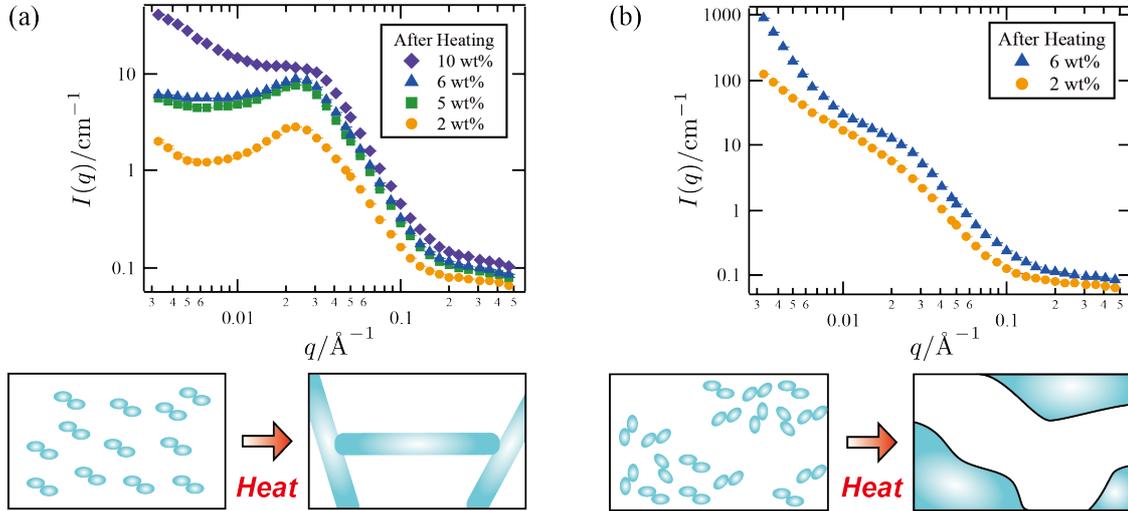

Figure 5. SANS profiles after heating of (a) OVA and (b) pOVA solutions and proposed gelation mechanism.

IV. Inhomogeneity-free amphiphilic gels

From the research above, inhomogeneity-free nature of Tetra-PEG gels and structure control by hydrophilic / hydrophobic interaction was elucidated. By combining these concepts, structure control of inhomogeneity-free gels by tuning hydrophobicity was performed. By replacing amine-terminated tetra-arm PEG into amine-terminated PDMS, inhomogeneity-free amphiphilic gels were prepared through similar procedure of Tetra-PEG gels. When the solvent is toluene, both PEG and PDMS are dissolved and a homogeneous network is prepared. When the solvent is substituted by water, PDMS unit shrinks since PDMS is hydrophobic. This shrinkage induces microphase-separation. To prove this conjecture, the amphiphilic hydrogels were investigated by complementary use of SANS and small-angle X-ray scattering (SAXS). When the molecular weight of PDMS is small, a PEG-core and PDMS-shell structure was observed (Figure 6(a)). In addition, lamellar structure was also observed when the molecular weight of PDMS is large (Figure 6(b)). These results will open the door for the precise control of amphiphilic network structure.
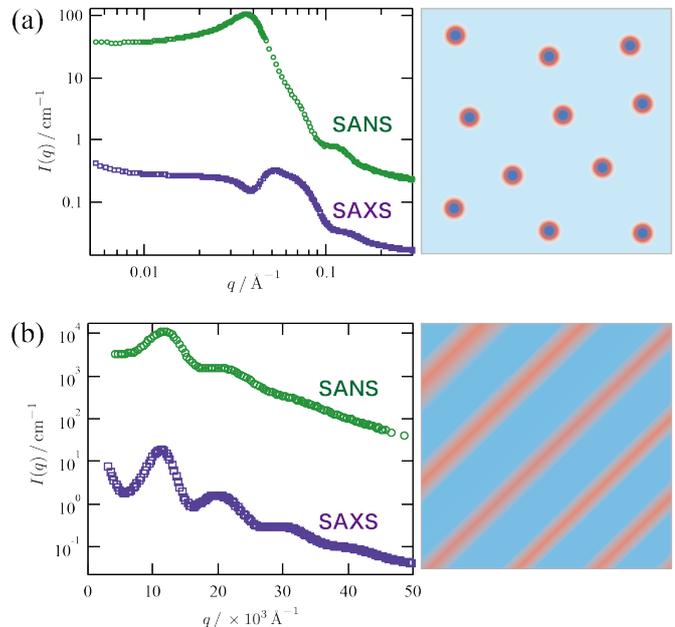

Figure 6. SANS and SAXS profiles and proposed structures of prepared amphiphilic hydrogels with (a) short PDMS and (b) long PDMS.