

論文内容の要旨

論文題目 Influence of the 2nd Component Distribution on Macroscopic Properties and Microscopic Structures of Polymer Gels

(高分子ゲル網目内の第二成分の分布の違いによる物性と局所構造の変化)

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1. Introduction

A polymer gel is a three-dimensional network, in which flexible polymer chains are connected by covalent chemical bonds or physical interactions. A polymer gel has the mechanical properties of a solid, even though it indeed may contain a large amount of liquid solvent. Owing to their versatility, polymer gels are used in many applications and among the most prominent soft matter materials. Introduction of some kind of additives or second component into the polymer chain networks is one of the commonly-used way to control the microscopic structures and macroscopic properties of polymer gels. The mechanical properties of polymer gels can be greatly changed as well as the interesting phase behavior like micro-phase-separation can occur due to the interaction between first network and the second component. There have been many studies that have reported the effect of second component into the polymer gels. These studies have generally discussed the total amount of second component and the resulting effect into polymer gels, in which the microstructures or macro-properties are tuned by changing the additive amounts of the second component. As far as we know, however, there have been little or no studies as to the effects of the spatial distribution of second component in polymer gels.

In this study, the effects of the second component distribution on the macroscopic properties and microscopic structures of polymer gels were investigated by using various experimental methods. We especially discussed the distribution of (i) ionization groups in charged gels and (ii) inorganic nanoparticles in hybrid gels, where the volume fraction of ionization groups or nano-particles was kept constant but the spatial distributions were different. In many cases, ionization process leads to a progress in transparency, swelling, and pH responsiveness. On the other hand, incorporation of inorganic nano-particle is generally carried out in order to improve the mechanical property. Therefore, we can manipulate these properties by tuning the second component distribution of polymer gels. We carried out swelling measurements and compressive measurements for macroscopic properties, dynamic light scattering (DLS) for the gelation dynamics, and small angle neutron scattering (SANS) for microstructure analysis.

2. Influence of Charge Distribution of Ionized Gels

2.1. Samples NIPAm/AAc copolymer gels

having different charge distributions were prepared as shown in Figure 1. These three types of gels have the same monomer concentrations of AAc (32mM) and NIPAm (668mM), but different spatial configurations of AAc groups. (a) and (c) were redox-polymerized gel while (b) was UV-polymerized one. The sample codes are Redpx-mono for (a), UV-poly for (b), and Redox-poly for (c).

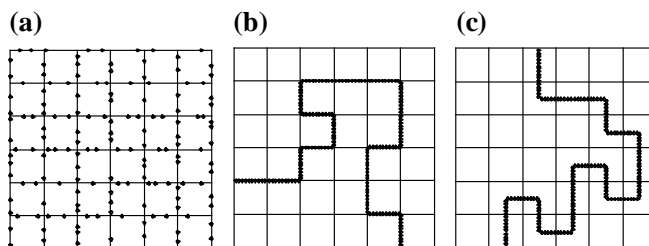


Figure 1. Diagram models of NIPAm/AAc gel networks: In (a) and (b), AAc groups (thick parts) were copolymerized in monomer and polymer units, respectively. In (c), the AAc polymers were interpenetrated in gel network but not cross-linked.

2.2. Results and Discussion

Figure 2 shows T dependence of swelling behavior for the three types of gel, with the swelling curve of redox-polymerized NIPAm (Redox-NIPAm) as a reference. Redox-mono showed the highest swelling degree and transition temperature, i.e., the highest ionization effect. UV-poly showed the little ionization effect due to the localization of AAc groups. Redox-poly showed the almost same behavior as Redox-NIPAm.

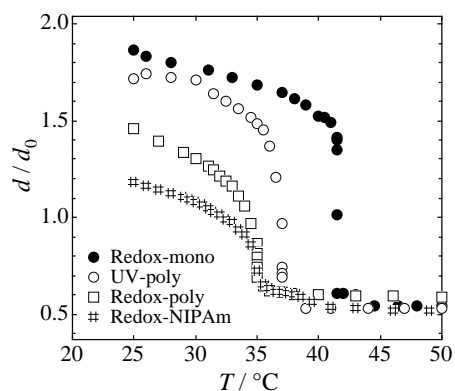


Figure 2. T dependence of swelling behavior of three types of NIPAm/AAc gel.

Figure 3 shows the T dependence of SANS profiles, $I(q)$

of each NIPAm/AAc copolymer gel. At a lower temperature range, it should be noted that $I(q)$ of UV-poly is extremely larger than the others, indicating the large static inhomogeneities. At a higher temperature

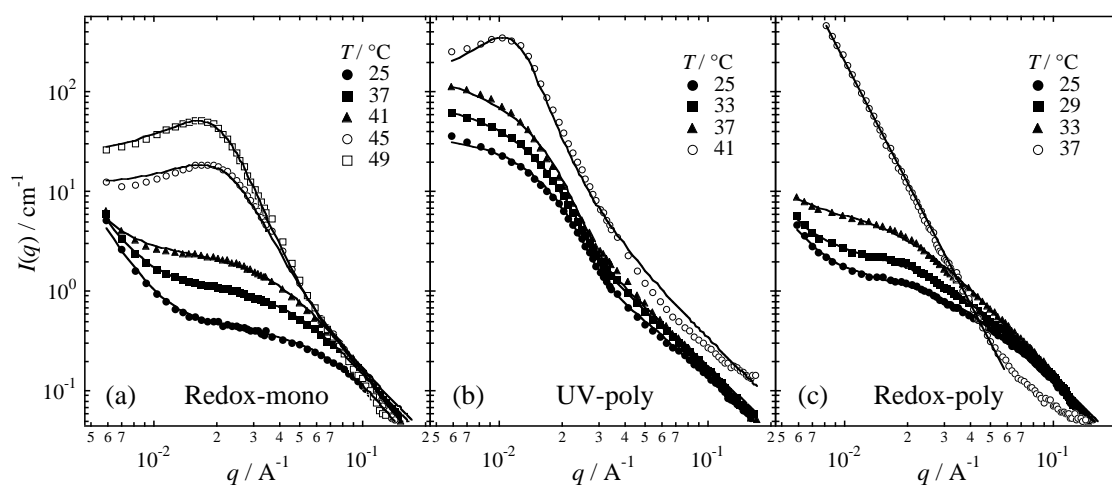


Figure 3. T dependence of SANS profiles, $I(q)$, for each type of gel network consisting of NIPAm and AAc. Solid lines show theoretical fitting curves.

range above the transition temperature, scattering peaks appeared in Redox-mono and UV-poly indicating the micro-phase-separation. The peak position of Redox-mono was higher than that of UV-poly, indicating a shorter periodical length due to the uniform distributions of AAc groups. $I(q)$ of Redox-poly showed the similar behavior to that of NIPAm homo-polymer gel.

We also investigated the pH dependence of swelling degree for each gel at 25 °C. The pH dependence was observed in the following order ; Redox-mono, UV-poly, and Redox-poly. This result directly indicates ionization effect of each gel.

3. Influence of Nano-particle Distribution of Organic/inorganic Hybrid Gels

3.1. Samples Three types of NIPAm/silica hybrid gels, which include different-sized silica spheres, were prepared. The volume fraction of the silica spheres and that of NIPAm were fixed at 0.011 and 0.0564 (= 700mM), respectively. The sample codes of hybrid gels were NS_L, NS_M, and NS_S in order of silica size.

3.2. Results and Discussion

Figure 4 shows the time evolution of the time-averaged scattering intensities observed at the scattering angle of 90°, $\langle I \rangle_T$, and the initial amplitude of the ICF, σ_I^2 . The increase of $\langle I \rangle_T$ means the aggregation process of silica particles because the scattering of silica is much higher than that of NIPAm. The instantaneous increase of $\langle I \rangle_T$ at $t = 20$ min indicates the rapid aggregation due to the large number density of silica spheres. On the other hand, the aggregation of silica became delayed with the increase of silica size.

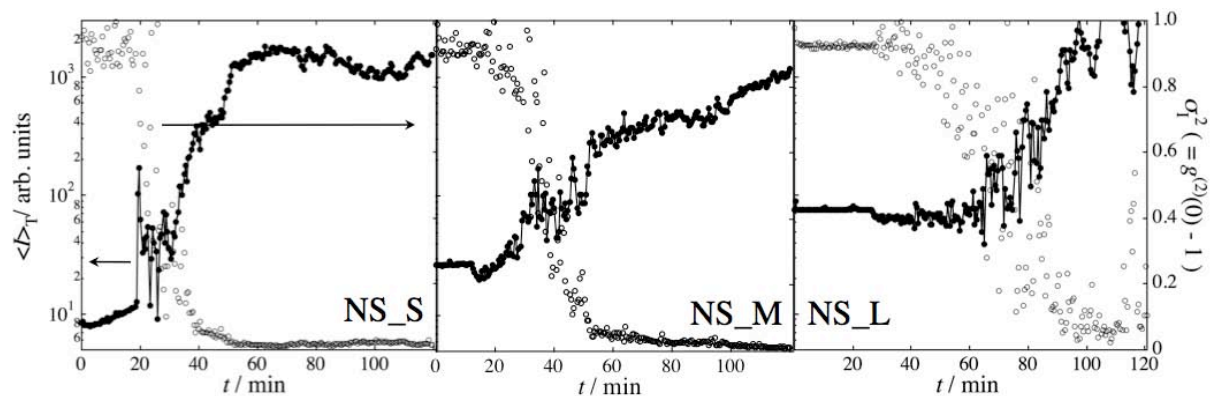


Figure 4. Time evolution of the time-averaged scattering intensities, $\langle I \rangle_T$, and the initial amplitude of the time-intensity correlation functions (ICF), σ_I^2 , for (a) NS_S, (b) NS_M, and (c) NS_L. $\langle I \rangle_T$ and σ_I^2 are designated by closed and open circles, respectively.

Figure 5 (a) - (c) show contrast-variation SANS results of the partial scattering functions for NS_S, NS_M, and NS_L. Here, (a) $S_{ss}(q)$, (b) $S_{sp}(q)$, and (c) $S_{pp}(q)$ indicate the self-terms of the silica, the cross-terms between the silica and the polymer, and the self-terms of the polymer, respectively. The solid lines indicate the theoretical fitting curves. The power law of $S_{ss}(q)$ in the low- q region indicates the fractal-like

aggregated structure of silica particles. Moreover, the positive sign of each $S_{sp}(q)$ indicates the attractive interaction between silica and polymer, which was quantitatively evaluated by the theoretical curve fitting.

Figure 6 shows a schematic model of the size dependence of NIPAm/silica hybrid gels. The silica spheres and polymer network are designated by black spheres and gray lines, respectively. The polymer chains that are adsorbed onto silica surface are indicated by the gray area. When the silica particle size is small, silica aggregation precedes NIPAm polymerization, and then the adsorption of the

NIPAm polymer onto the silica surface takes place. The thus-estimated microstructure is shown schematically in Figure 6(a), where larger elastic modulus was observed. As the size of the silica particles increases, aggregation of the silica spheres becomes delayed during the gelation process, and the aggregation period overlaps the polymerization period of NIPAm. The adsorption of the NIPAm polymer onto the silica surface occurs concurrently during the gelation process. That is, the final obtained structure is characterized as shown in Figure 6(b).

4. Conclusion

We presented the possibility of new method to tune the macro-properties and microstructures of polymer gels by focusing on the second component distribution in polymer gels. That is, the localization of ionization in charged gels was found to play an important role in the mechanical properties, leading to the decrease of the ionization effect. In addition, it was clarified that the nano-structures of hybrid gels can be manipulated by controlling the balance between the aggregation of inorganic materials and polymerization of organic compounds. We hope that this study would contribute to the development and designing of further excellent polymer gels.

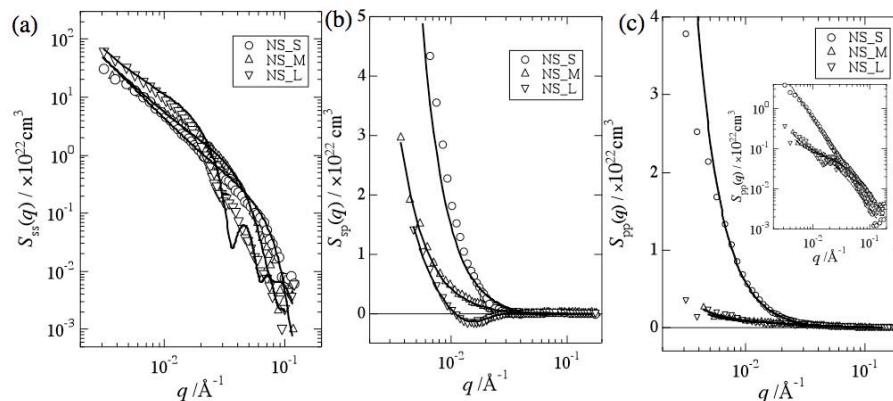


Figure 5. Partial scattering functions for (a) the self-terms of silica, $S_{ss}(q)$, (b) the cross-terms between silica and polymer, $S_{sp}(q)$, and (c) the self-terms of polymer, $S_{pp}(q)$ for NS_S, NS_M, and NS_L. The inset of (c) is the double logarithmic plot for $S_{pp}(q)$.

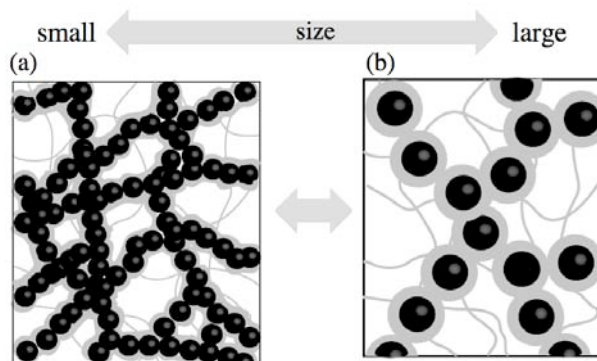


Figure 6. The size dependence of the schematic models of NIPAm/silica hybrid gels.