Structural analysis of lipophilic polyelectrolyte gels in non-polar solvents

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Ionic hydrogels prepared by crosslinked polyelectrolytes have been known as superabsorbent polymers that swell and absorb water several hundreds times as much as their dried state. They are used in widespread applications such as diapers, fillers in cosmetics, separation media, drug delivery systems, biomedical devices, sensors, inks, and display devices. The high swelling abilities originate from the electrostatic repulsion and osmotic pressure between the interior and exterior of gels induced by freely mobile counterions in the networked polyelectrolytes. On the other hand, in most organic solvents, except highly polar ones, the polyelectrolyte gels collapse or shrink because of aggregation of ions compared to the dried gels. Moreover, swelling degree of nonionic crosslinked lipophilic polymers in organic solvents is not so high, as a result of lack of enhancement induced by ionic dissociation. Thus, the development of superabsorbent polymers for such organic solvents still remains unsolved.

In 2007, a first example of lipophilic polyelectrolyte gels as superabsorbent polymers that swell with a high degree in less-polar or nonpolar organic solvents ($3< \varepsilon <10$, where ε represents dielectric constant) were developed by Ono et al. (T. Ono, T. Sugimoto, S. Shinkai, K. Sada, Nat Mater. 2007, 6, 429.) Their design was based simply on incorporation of a small amount of the lipophilic ionic groups dissociable in the media into the poly(octadecyl acrylate) gels. Substituted tetraphenylborate as a lipophilic anion and tetraalkylammonium with long alkyl chains as a lipophilic cation were selected as ionic groups. This gel is expected as an effective way to improve environmental issues, such as recovery of discharged oil and volatile organic compounds (VOCs).

In our research, we conduct detailed structural analysis on this gel by using small angle neutron scattering (SANS) in order to clarify a high swelling mechanism.

To achieve this purpose, we investigated effects of ionic groups on internal structure of the solution state. Figure 1 shows polymer concentration dependence of SANS profiles. We found that both of these polymers formed cylinder-like shape because these SANS profiles could fit by cylinder shape function. In addition to this, inhomogeneity of an ionized system increases with an increase of the polymer concentration. We think that this inhomogeneity corresponds to the clusters because we confirmed the presence of cluster in the ionized system by using dynamic light scattering in a previous research. Moreover, from fitting analysis, it is revealed that osmotic pressure of lipophilic polyelectrolyte is larger than that of the neutral system, which leads to a high swelling ability of lipophilic polyelectrolyte gels.

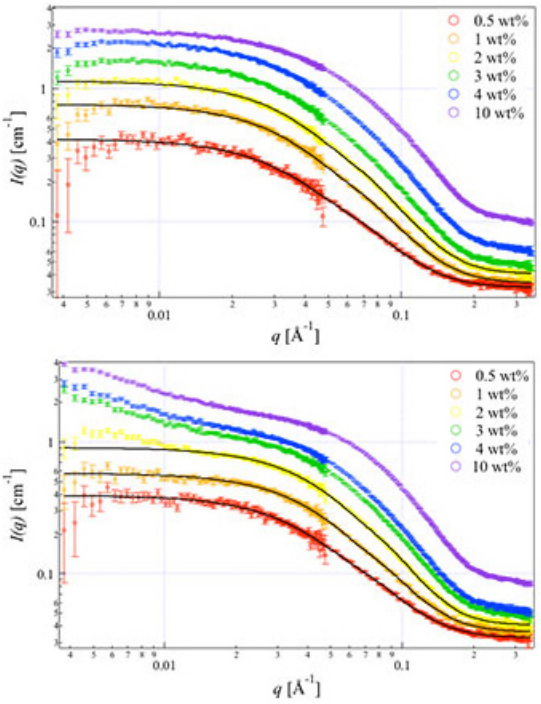

Fig. 1. SANS profiles of (upper) neutral poly(octadecyl acrylate) solution, (lower) lipophilic polyelectrolyte solution.