Structural analysis of entanglement networks of ultrahigh molecular weight ion gels

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Ion gels, which are polymer gels using ionic liquids as solvents, are expected to be applied as gel electrolytes with high safety and stability in next-generation electrochemical devices. For such applications, the mechanical strength of the gel electrolyte is essential. However, achieving high mechanical strength in polymer gels has typically required advanced polymer synthesis techniques and complex processing methods.

Recently, we developed ion gels formed by the entanglement of ultrahigh molecular weight polymers in ionic liquids using a facile one-pot method.[1] These ion gels exhibit superior mechanical properties compared to conventional chemically cross-linked ion gels. Moreover, since no chemical cross-linking agents are used, the gels can be recycled through a hot-pressing process. Notably, it was found that the ion gel composed of ultrahigh molecular weight PMMA and the aprotic ionic liquid [C_2mim][TFSI] demonstrates rapid self-healing at room temperature. However, the origin of its high stretchability and self-healing properties has not yet been elucidated from the perspective of its microscopic structure.

In order to elucidate the nano-scale structure of our ion gels, we have performed the small-angle neutron scattering (SANS) measurements for our ion gels from physical entanglements with various molecular weights of PMMA. For comparison, we have also measured PMMA gels with chemical cross-linker. [C_2mim][TFSI] was used as a solvent. The measurements were performed with the sample-to-detector distances of 2 m and 12 m, which cover the range of 0.003 Å^{-1} < q < 0.3 Å^{-1}.

Figure 1 shows the SANS profiles of the ion gels. Red and blue symbols are the SANS profiles obtained from the ion gels made from physical entanglements. High-q region (0.05 Å^{-1} < q) for both profiles can be fitted by the Ornstein-Zernike function, which is used to evaluate the thermal concentration fluctuation. Low-q region (q < 0.01 Å^{-1}) for both profiles show the upturn, which indicates the existence of inhomogeneities. From the starting point of the upturn, it is suggested that the lower molecular weight of PMMA makes homogeneous ion gels.

Compared to the case of ion gels from physical entanglements, the scattering from the ion gels made from chemical cross-linker (green and yellow symbols in Figure 1) is strong. This result can be interpreted that the permanent crosslinking introduces the inhomogeneity in the gel while the structural stress introduced in the gels made from physical entanglements can be relaxed via the reptation of the polymers.

[1] Y. Kamiyama *et al.*, *Sci. Adv.* **8**, eadd0226 (2022).

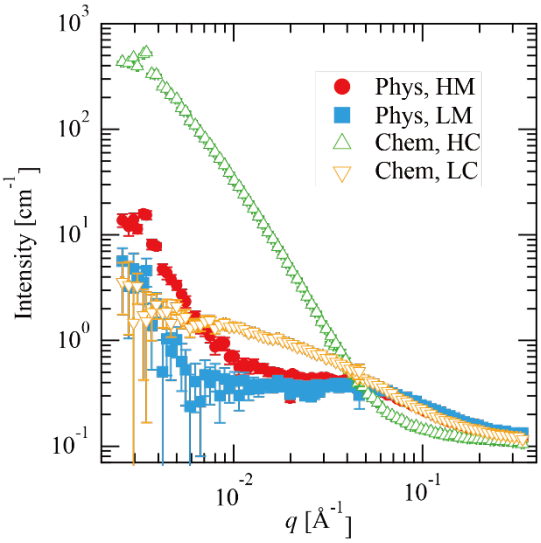

Fig. 1. SANS profiles of ion gels from physical entanglements with high (red) and low (blue) molecular weight PMMA and from chemical cross-linker with high (green) and low (yellow) cross-linker concentrations.