

Structural study on the "nonswellable" hydrogel

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Hydrogels are an important class of soft materials particularly in the medical and bio-science fields. In general, hydrogels swell with water due to the osmotic pressure imbalance inside and outside the gel. Swelling leads to a significant mechanical deterioration and volume expansion, which may cause serious damage to the surrounding tissues when the gel is used in the body.

Recently, we developed a nonswellable thermo-responsive hydrogel synthesized by end-linking between four-armed poly(ethylene glycol) (Tetra-PEG) and four-armed poly(ethyl glycidyl ether-co-methyl glycidyl ether) (Tetra-PEMGE). While PEG is a well-known hydrophilic polymer, PEMGE is a thermo-responsive polymer exhibiting lower-critical solution temperature (LCST) type phase behavior in aqueous solution. When the hydrogel was heated above a certain transition temperature, Tetra-PEMGE units became hydrophobic and started to shrink, resulting in macroscopic shrinking of the entire hydrogel. In the previous study, we found that the equilibrium swelling ratio of the hydrogel was ca. 300% at 10 °C, whereas it decreased dramatically to be ca. 100% at 37 °C, i.e. the physiological temperature. Hence our hydrogel was practically nonswellable in the human body. Interestingly, the hydrogel remained transparent even after shrinking of Tetra-PEMGE units, indicating the formation of a structure with the length scale much smaller than the visible light wavelength. In the present experiment, we carried out small-angle neutron scattering (SANS) measurements on the nonswellable hydrogel to clarify the structural origin of its nonswellable feature.

SANS measurements were performed using QUOKKA at the OPAL reactor in

ANSTO, Australia, with the wavelength of 5 Å and each of three different sample-to-detector distances of 1.3, 8, and 20 m. The sample temperature T was controlled by the 20-position temperature-variable sample changer. The SANS profiles were corrected for absorption, cell scattering, and solvent scattering. To avoid complications in the model fitting process, the data were further corrected for instrumental smearing by an iterative desmearing algorithm.

Fig. 1 shows the representative SANS profiles of the nonswellable hydrogel at various temperatures. At T lower than 16.6 °C, the profiles are simple; they contain an upturn in the low- q region and a shoulder in the high- q region. The upturn in the low- q region is due to the large-scale aggregation of PEG end-groups and has been observed even in aqueous solutions of PEG. The shoulder in the high- q region reflects the concentration fluctuation of the polymer network and can be explained by the Ornstein-Zernike function, as shown with the solid curves in Fig. 1. However, at T higher than 19.5 °C, an intense peak emerges in the low- q region, which is accompanied by an additional shoulder and small peak in the high- q region at even higher temperatures. The SANS profiles suggest that a nanometer-scale discrete domain structure is formed upon shrinking of Tetra-PEMGE units. The low- q peak and high- q features should reflect the inter-domain correlation (structure factor) and intra-domain correlation (form factor), respectively.

We performed the model fitting analysis on the SANS profiles to extract quantitative information on the domain structure. The spherical domains with the modified hard-sphere interaction were assumed. The model scattering function, shown with the solid curves in Fig. 1, successfully explains

the experimental SANS profiles particularly in the high- q region. We estimated the mean aggregation number N , defined as the number of four-armed prepolymer units contained in one spherical domain, from the structural parameters obtained by model fitting. Strikingly, N was 14 - 21, which was much larger than unity. This clearly indicates that multiple Tetra-PEMGE units as well as Tetra-PEG units aggregate into a single spherical domain. The formation of such relatively large domains causes the significant distortion of the network in the matrix phase, rendering our hydrogel nonswellable.

In summary, we investigated the microscopic structure of the nonswellable hydrogel using SANS and revealed that the formation of spherical domains each containing multiple prepolymer units was responsible for the nonswellable feature. The findings in this experiment will help designing the nonswellable hydrogels and contribute to fundamental understanding of amphiphilic polymer network systems.

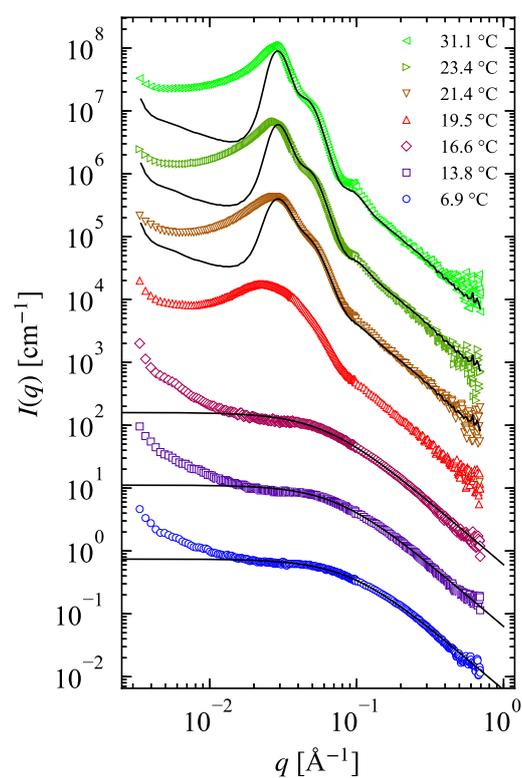


Fig. 1. SANS profiles of the nonswellable hydrogel at various temperatures. Solid curves represent the fitting results.