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Thermoresponsive structural change in porous PEG/PNIPAm binary gels

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1 Introduction

Much attention has been given to polymer gels due to their potentiality for intelligent biocompatible materials. We have been studying radiation-induced fabrication of polymer gels with complicated structure, such as multi - component gels and porous gels. The merit of radiation-induced reaction in the preparation of polymer gels is that chemical additives such as reaction initiators, crosslinkers, or catalysts, are unnecessary, which leads to the reduction of impurities in final product gels. Moreover, it is also known that radiation-prepared gels show less structural inhomogeneity. Those advantages are favorable for fabricating advanced functional materials made of polymer gels.

Until now, we have succeeded in preparing binary gels composed of poly(ethylene glycol) (PEG), a common polymer for hydrogels, and poly(N-isopropyl acrylamide) (PNIPAm), a well-known thermoresponsive polymer, by the two-step γ-ray irradiation method, and their porous gels have also been synthesized in the same way as these binary gels. Swelling behavior of these gels were already investigated. The swelling experiments demonstrated that radiation-prepared binary gels are also shrunk in the same manner as PNIPAm gels, and the degree of shrinking is smaller for porous gels in comparison with nonporous gels. From this result, it is suggested that PNIPAm chains in the porous gels are localized in the pore space. However, more direct evidence was needed to prove that picture. Therefore we employed the small-angle X-ray scattering (SAXS) measurement to clarify nano-meter scale structure of those gels.

In this report, we describe the SAXS analysis of radiation-prepared PEG/PNIPAm binary gels at temperatures lower and higher than LCST of PNIPAm.

2 Experiment

A PEG aqueous solution (10 wt%) was irradiated with a 60-kGy dose of γ-rays at a dose rate of 1 kGy/h in the absence of oxygen, and a PEG matrix gel was obtained. Then, a NIPAm monomer solution was impregnated into the PEG matrix gel and after that γ-rays (3 kGy at 1kGy/h) were irradiated to it again. After purification, a PEG/PNIPAm binary gel was obtained. In the porous gel preparation, silica microparticles (200 nm and 1000nm in diameter) were mixed into the PEG aqueous solution under ultrasonic irradiation and then decomposed by the HF treatment after the PEG gelation.

The SAXS experiment was done at BL-10C, Photon Factory. The samples gels that were fully swollen in the water was placed in the measurement cell and scattering data were collected at several temperatures ranging from 20–40 °C.

3 Results and Discussion

Figure 1 shows scattering profiles of PEG/PNIPAm binary gels in the swollen state. At 20 °C, lower than LCST of PNIPAm, all the scattering profiles are almost the same irrespective of the presence of the pores. These profiles are also similar to that of a pure PEG gel. This fact indicates that there is little structural difference among those gels in the swollen state.

When the temperature is raised above LCST of PNIPAm, the scattering profiles becomes quite different from the above result. Although the pure PEG gel shows no definite change at 40 °C, PNIPAm-incorporated gels give scattering profiles with steep rise in the low q region. This clearly exhibits that PEG gels become thermoresponsive due to radiation-incorporation of PNIPAm chains. However, the steep rise observed in the low q region is different among three scattering curves shown in Figure 1. The slope value of the low-q rise for the two porous gels are larger than that for the nonporous gels. The rise curves for the porous gels are well fitted with the $I \propto q^{-4}$ relationship, Porod's law. From this fact, we can say that porous gels have clear phase-separated structure at higher temperatures, which suggests that PNIPAm chains are localized in the pore space.

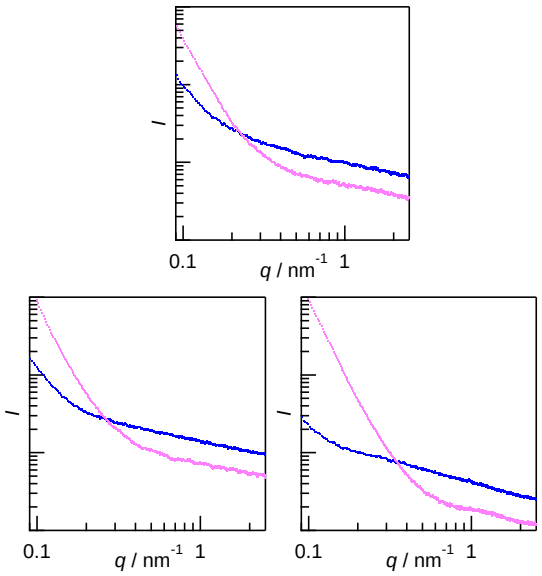

Figure 1. SAXS profiles of PEG/PNIPAm binary gels in the swollen state. The blue and red lines correspond to 20 and 40 °C, respectively. (Top) nonporous gel, (Bottom left) small-pore gel, and (Bottom right) large-pore gel.

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