

Thermoresponsive behavior of radiation-fabricated porous binary hydrogels as revealed by small-angle neutron scattering

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The gamma-ray-induced preparation of polymer hydrogels has the advantage of reducing residual impurities and structural inhomogeneity in the gel compared with those prepared by chemical crosslinking. We have so far been studying radiation-prepared binary polymer hydrogels composed of polyethylene glycol (PEG) and poly (N-isopropylacrylamide) (PNIPAm), which is aimed at incorporating thermoresponsive property into a common polymer hydrogel. PEG is well known as a common polymer forming hydrogels, while PNIPAm as a thermoresponsive polymer to form hydrogels exhibiting volume transition around 34 degrees Celsius. In this study, hydrogenated PNIPAm (hPNIPAm) was incorporated into deuterated PEG (dPEG) matrix gels by gamma-ray irradiation, and then the nanoscale structural change of the dPEG/hPNIPAm binary hydrogels induced by temperature change over the transition temperature of PNIPAm was investigated by contrast-variation small-angle neutron scattering. dPEG/hPNIPAm binary hydrogels were prepared as follows. A 9.8 wt% D₂O solution of fully deuterated PEG was irradiated with gamma rays to yield dPEG matrix gels. After rinsing out unreacted polymers from the matrix gels, the dried matrix gels were swollen in a 10 wt% hPNIPAm H₂O solution and irradiated with gamma rays again to yield dPEG/hPNIPAm binary hydrogels. Porous matrix gels were also prepared by mixing silica microparticles before gelation and chemically decomposing them after gelation. SANS experiments were carried out at QUOKKA, a SANS instrument of OPAL, ANSTO. Gels were swollen in several compositions of D₂O/H₂O mixed solvents and torn into small pieces before putting in sandwich

cells. Measurements were performed at 25 and 45 degrees Celsius, which are below and above the transition temperature of PNIPAm, respectively.

Scattering profiles of porous dPEG/hPNIPAm gels in 0, 20, and 100% D₂O/H₂O mixed solvents are shown in the figure. The calculation of scattering length density indicates that contrast of hPNIPAm is almost zero in 20% D₂O solvent. Therefore, the scattering profiles in 20% D₂O show only the structure of dPEG matrix gels, and the deviation from the scattering profile of 20% D₂O is largely due to the contribution of hPNIPAm scattering. In the profile of 20% D₂O, a shoulder appears near 6 inverse angstrom above the transition temperature, indicating that shrinkage of incorporated PNIPAm chains induces the interference of PEG chains in the matrix gel. In 100% D₂O above the transition temperature, the scattering intensity obeys the relationship of -4th power of scattering vector, Porod's law, suggesting that PNIPAm chains form domains with clear interface with surrounding PEG matrix gels.

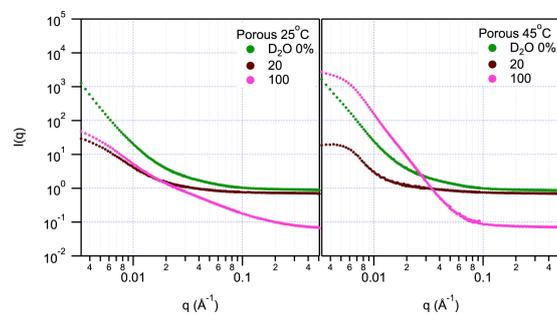


Fig. 1. Scattering profiles of porous dPEG/hPNIPAm binary hydrogels in various compositions of D₂O/H₂O mixed solvents below and above the transition temperature of PNIPAm.