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Humidity dependence of skeleton structure of Double network polymers

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1 Introduction

In this study, we focused on the mechanical properties of the living materials. Recently DN-polymers which were xerogel of double network hydrogels have cross-linked aqueous polymer networks obtaining unique mechanical properties [1]. The Young's modulus of the DN-polymers was nearly unchanged around 5×10^2 MPa in the relative humidity (RH) between 0% and 80%. When the RH was more than 80%, the Young's modulus drops 1/1000. To understand the origin of mechanical properties of the polymer structure and the role of the water molecules, we investigated using small angle scattering (SAS) techniques. By complementary use of X-ray and neutron namely SAXS and SANS, the humidity dependence of skeletal structure of hydrophilic materials, DN-polymers and behavior of adsorbed water molecules were determined.

2 Experiment

The porous polymeric xerogels DN-poylmers were prepared by freeze-drying of synthetic polymer gels (DN gels). DN-gels [3,4] were polymerized by 2-acrylamide-2-methyl-propanesulfonicacid sodium salt (NaAMPS) and acrylamide (AAm), with a cross-linker, *N,N'*-methylene bisacrylamide (MBAA).

The SAXS were performed at BL10C. Wavelength was 0.097 nm and sample to detector distance was 1 m. The exposure time was 15 secs. The *q*-scale correction had done by silver behenate powder (Eastman Kodak, Inc.), and glassy carbon ("H16") kindly provided from Ilavsky. J. was used as a standard to calibrate the scattering intensity [9]. Irena was used for data reductions [10].

Samples ($5 \times 5 \times 0.4$-mm^3) were set in a vacuum chamber having both upstream and downstream windows with kapton film (50-μm thickness). The chamber was placed under a vacuum using the turbo molecular pump. The pressure of sample was 0.0 Pa, and was monitored with a pressure gauge. The RH (p/p_0) was controlled by absolute pressure p and saturated wter pressure p_0 in the chamber. The p was controlled by valve operation to the chamber. The measurements were performed under 25 °C.

3 Results and Discussion

We determined nanoscale structure change against RH using small angle X-ray scatering under RH < 80%. In the case of X-ray scattering, scattering from light elements, such as hydrogen atoms are small in particular. Therefore scatteing profiles would be regaraded mainly from polymer network structure.

Figure 1 shows scattering intensity of the DN-polymers from SAXS. When the RH was 0–80%, The profiles did not have obvious RH dependence. The intensity difference is in 3% at low $q = 0.02$ Å^{-1}, and 2% at $q = 0.3$ Å^{-1}. The power of the scattering profiles were less than −3 at $q < 0.02$ Å^{-1}. Supposing the scattering at $q < 0.02$ Å^{-1} is from surface scattering, and the relation, $I \propto q^{(-6-Ds)}$ was adopted for fractal dimension *Ds* estimation. The values were approximately 2.6 and had no obvious RH dependence. The SAXS results also showed the DN-polymers are isotropic materials in length scale range from 2 to 60 nm.

From the SAXS analysis, we regards that the scattering intensity is from surface scattering. The slopes of the q range $q < 0.02$ Å^{-1} were not change a lot against RH. This unique property on hydrophilic DN-polymers was also shown macroscopically as little size change by optical microscopy. The skeletal structure of the DN-polymers at this q range does not change. We could ignore exact size change for the first approximation, to engage further SANS analysis. This was big step in order to approach the origin of the origin of the mechanical properties of DN-polymers.

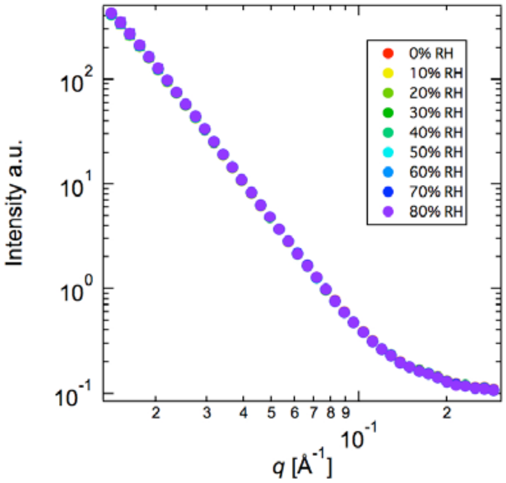

Figure 1: Humidity dependence of SAXS profile of DN-polymers at room temperature

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References

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