Nuclear Resonant Scattering Study of the Dynamics in Polymer Gels

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Gels show unique properties because of the interaction between the two constituents, the polymer network and solvent. Among the fascinating phenomena, the authors have been much interested in the property evolution when the solvent is being taken away. One of the characteristic feature of the gel during the dehydration process which was observed in the previous studies is that the log weight decreased almost proportionally to time; the slope altered at a certain time (t_g') showing a turning point from the loss process of the free water to that of the bound water. The elastic property of the gel also showed a clear anomaly during the dehydration process, as well as the weight and volume; the complex-elastic-stiffness amplitude increased up to 10^3 times the initial value around t_g', and the elastic loss-tangent (tan δ) showed a clear peak just before t_g'. This feature resembled the elastic change of non-crystalline polymers in the glass transition by the drop of temperature. The similarity can be explained as follows: the free water loss in the dehydration process brings the network polymer chains close to each other by the capillary force of the residual free water in the gel, therefore, the increasing interaction between the neighboring network chains will hinder their thermal motion in the similar situation to the freezing mechanism of micro-Brownian motion with decreasing temperature in the glass transition of the non-crystalline polymers. In such situation, the DTA measurements of the dehydrated heat-treated egg white gel were performed with elevating temperature. By the measurement, an endothermic peak was found, whose intensity and temperature became higher with increasing temperature elevation rate. Because these characteristics are usually observed in the glass transition, the dehydrated gel could be identified as a "glass." As well as the thermal analysis, there can be other methods by which the investigation of the glass state can be performed. In the previous study, we characterized the dehydration process of the PAAm gel by examining the Raman scattering spectrum both in the low (from 0 to 550cm^{-1}) and high (above 550cm^{-1}) frequency regions, simultaneously with the weight measurement. Remarkable change in the spectrum was also observed in the low frequency region. In the early stage of the dehydration, a diffusive central mode was observed, however, as the dehydration proceeded, the diffusive mode became narrower, and after t_g', the mode became negligible and a pair of side-band peaks emerged. Such peaks are well-known as the Boson peak which commonly exists in the low lying Raman spectrum of the glass and amorphous materials, therefore, we could confirm that the PAAm gel became a glass by the dehydration, from the spectroscopic point of view. The Boson peak was also observed in the dehydrated heat treated egg white gel. Under suchi condition, in the present study, we observed nuclear resonant scattering from the N-isopropylacrylamide/sodium acrylate copolymer gel which contains ferric ion. From the measurement, we have got the spectra shown below (preliminary version). Further analyses are in progress.