Compressed-Exponential Relaxations in Trehalose Glass

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Summary

We measured the $\alpha$-relaxation in trehalose glass by using photon correlation spectroscopy (PCS). The $\alpha$-relaxations of trehalose glass showed a crossover from stretched-to compressed-exponential relaxations as the temperature increased. From the Raman scattering measurements, we found that the unusual compressed-exponential relaxation in trehalose glass was caused by the change of glycosidic linkage structure in trehalose molecule.

1. Introduction

There are many strategies in nature for long-term survivals of organisms and a bio-protect effect is one of the most interest among those long-term survival processes. The stabilizing role of trehalose on biomolecules has been recognized for many years in biological, pharmaceutical and food sciences[1, 2, 3, 4]. A $\alpha, \alpha$-trehalose composed by two molecules of glucose is a well-known non-reducing disaccharide that is commonly found in yeast, fungi, bacteria, mushroom, and desert plants, and is known as the most effective sugar for protecting the bio-molecules. However, the origin of the protection mechanism is still remaining as an open question and there are various opinions about the protection mechanism in trehalose glasses[5, 6, 7].

In this study, we are interested in the relaxation process of trehalose glass. The study of the relaxation process of trehalose glass is an interesting topic to understand the dynamics of molecules in a glass state. We believed that it will be helpful to understand the protection mechanism of trehalose glasses.

2. Experiments

Trehalose dihydrate was sponsored by Cargill Corporation and dried by using moisture analyzer(Sartorius MA100, Germany) at 130 °C for 5 hours. The trehalose glass was made by using microwave oven[8] because the microwave oven is an effective method to heat the trehalose quickly and uniformly without caramelization process during the heating.

In a photon correlation spectroscopy (PCS) experiment, the Brookhaven BI-9000AT digital correlator (Brookhaven Instruments Corp., U.S.A.) was used. The $|\phi(t)|^2$ of depolarized components for different temperatures from 110 °C to 180 °C is shown in Fig. 1. The solid lines are the fits to the square of stretched-exponential function.

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used to measure the correlation function, $G(t)$, of trehalose glass. The Brookhaven correlator can cover ten decades of time ($10^{-1} \mu s \sim 10^9 \mu s$). The incident beam was a vertically polarized 514.5 nm green light of Ar-ion laser (I90-C, Coherent, USA) with 200 mW power and single mode fiber optic was used for detecting the scattered light. The depolarized (VH) components of the scattered light were selected by a Glan-Thompson Analyzer with a leakage factor of less than 1%. A scattering geometry was 90°. The time range used in this study was $10^3 \mu s \sim 10^8 \mu s$ and the scattering wave number $q$ was fixed at $2.4 \times 10^5$ cm$^{-1}$ ($\theta = 90°$).

In a Raman spectroscopy measurement, the back-scattering geometry was used. The incident beam was a vertically polarized 514.5 nm green light of Ar-ion laser (I90-C, Coherent, USA) with 100 mW power. The scattered light was measured by using monochromator (Acton Research, Spectra Pro-750, USA) and charge coupled device (AndorMCD, USA) in the scattering wave vector range of 1000~1200 cm$^{-1}$.

3. Results & Discussion

We measured the $\alpha$-relaxations in trehalose glass by using photon correlation spectroscopy (PCS) at temperatures ranging from 110 °C to 180 °C. Figure 1 shows the $|\phi(t)|^2$ of VH components in trehalose glass. The symbols are experimental results and the solid lines are the fits to the square of stretched-exponential function

$$|\phi(t)|^2 = f_c^2 \exp\left(-2(t/\tau)^\beta\right)$$  \hspace{1cm} (1)$$

with fitting parameters, non-ergodicity parameter $f_c$, relaxation time $\tau$, and stretched exponent $\beta$.

Figure 2 shows the stretched exponent $\beta$ of trehalose glass at temperatures ranging from 110 °C to 180 °C. The stretched exponent $\beta$ increased with increasing temperature and the slope was changed around 140 °C. Moreover, the stretched exponent $\beta$ is bigger than 1 above 140 °C. This result indicates that the relaxation process of trehalose glass changed from stretched- to compressed-exponential relaxations around 140 °C. While such compressed-exponential relaxation with $\beta > 1$ may seems unusual, similar behavior has been observed on a number of soft solids including colloidal gels[9], micellar polycrystals[10], and clays[11]. Recently, Bouchaud and Pritard[12] suggested a specific model about the compressed-exponential relaxation which associates with the local rearrangement or micro-collapse of particles. In this study, we believe the compressed-exponential behavior in trehalose glass was caused from a intra molecular structure change of trehalose molecule based on the X-ray diffraction experiment results which will be described in another publications.

We expected that the structure change in trehalose molecule may originated from the change of out-of-ring vibrations (glycosidic linkage) between glucose molecules. To find the change of out-of-ring vi-
bration, we measured the Raman spectra of trehalose glass in the wavenumber range of 1000–1200 cm$^{-1}$ because the Raman scattering spectra of trehalose glass shows the out-of-ring vibrations (glycosidic linkage) around 1140–1150 cm$^{-1}$ due to the coupling of C-O stretching ($\nu$ (C-O)), C-H bending ($\delta$ (C-H)), and C-O-H stretching ($\nu$ (C-O-H)) modes[13].

Figure 3 shows the Raman spectra of trehalose glass at different temperatures. We fitted the data by using Equation (2) that the convoluted Lorentzian functions with a Gaussian-shape laser line.

$$I(\omega) = I_0 + \frac{2A\mu}{\pi} \frac{\Gamma}{4(\omega - \omega_c)^2 + \Gamma^2} + \frac{(1 - \mu)\sqrt{4\ln 2}}{\sqrt{\pi}\Gamma} \exp\left(-\frac{4\ln 2}{\Gamma^2}(\omega - \omega_c)^2\right).$$

Here, $I(\omega)$ is the intensity of scattered light, $\mu$ is an adjustable parameter which depends on the instrument factor, $\Gamma$ is a damping factor related to the bulk and shear viscosity of the system, $\omega$ is the frequency, and $\omega_c$ is the position of the Brillouin shift.

Figures 4 shows the Raman peak shift of trehalose glass[14]. The Raman shift showed a constant value at the temperature range 40 °C $\sim$ 135 °C and started to decrease at the temperature around 135 °C. It indicates that the glycosidic bond of trehalose molecule was changed around 135 °C. From this result, we concluded that the unusual compressed-exponential relaxation in trehalose glass maybe caused by the change of glycosidic linkage structure in trehalose molecule.

4. Conclusions

We measured the $\alpha$-relaxation in trehalose glass by using photon correlation spectroscopy (PCS) at temperatures ranging from 110 °C to 180 °C. The $\alpha$-relaxations of trehalose glass showed a crossover from stretched- to compressed-exponential relaxations as the temperature increased. From the Raman scattering measurements in the range of 1000–1200 cm$^{-1}$, we found that the slope of Raman shift was changed around 135 °C. From this result, we concluded that the unusual compressed-exponential relaxation in trehalose glass maybe caused by the change of glycosidic linkage structure in trehalose molecule.

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References


