Spectroscopic Evidence of Phase Transition of Monomolecular Water in Solid Polystyrene

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Abstract   Phase transition behavior of monomolecular water in solid polystyrene was examined by temperature variable Fourier transform infrared spectroscopy. Spectral changes showed, for the first time, that monomolecular water in a polymer matrix (in a closed system) could be condensed and then frozen and also that the ice formed could be grown and diminished by vapor deposition in cooling process and sublimation in heating process, respectively.

Keywords: Polymer Solid, Phase Transition, Monomolecular Water, Infrared Spectroscopy

Several recent studies on adsorption/adhesion of materials on polymer solid – water interfaces have suggested that the structure (physicochemical properties) of water on the surface is a key for determining the origin of the adsorption.[1] To determine the origin, many researchers have examined the structure of water in polymer–water systems by thermodynamic methods.[2] Water in hydrated polymer systems is roughly categorized into three types based on calorimetric measurement: free water, freezable bound (FB) water, and non-freezable bound (NFB) water.[3] In most studies, based on the assumption that "phase transition is ordinarily from gas to liquid and then to solid", exo/endothermic peaks around 273 K have tended to be assigned to *freezing*/*melting* events of water. A general understanding of sorbed water into polymer solids is that the amounts of free water and FB water decrease with a decrease in water content and they finally disappear. The amounts of sorbed water in a conventional environment (~1 atm, ~300 K, ~60 %RH) is very small, and all of it is therefore thought to exist as monomolecular water and to be NFB water.

On the other hand, a recent study[4] using molecular dynamics on a phase diagram of Lennard-Jones fluid (methane) in a nano cavity indicated that the triple point of the fluid was shifted to lower pressure and higher temperature (T). This means that, even in the case of extremely low water content, it is not always acceptable that there is no phase transition of the sorbed water. This prediction argues strongly against the widely accepted understanding of sorbed water.

In this study, using temperature-variable Fourier transform infrared spectroscopy, the thermal response of monomolecular water in a non-water-soluble polymer (polystyrene, PSt) was examined. The experimental results showed, for the first time, that monomolecular water in a polymer matrix (in a closed system) could be condensed and then frozen and that the ice formed could be grown and diminished by vapor deposition in cooling process and sublimation in heating process, respectively.

Figure 1A shows the IR spectrum of water sorbed into an annealed solid PSt with water content of 0.3 wt% at 298 K. The sorbed water had only two sharp peaks at 3671 and 3585 cm^{-1}, which are assigned to symmetric (ν_{1OH}) and anti-symmetric (ν_{3OH}) O–H stretching fundamentals, respectively.[5] A comparison with the spectrum of liquid water clearly indicates that the sorbed water does not form associated water (cluster). Additionally, the fringe-like patterns around 3765 and 3657 cm^{-1}, which were ν_{1OH} and ν_{3OH}, respectively, of gaseous water disappeared, and both the fundamentals shifted to a lower wavenumber. These spectral characteristics show that the sorbed water is restricted monomolecularly on a hydrogen-bonding (HB) site (phenyl ring).[6]

Based on the general understanding, any phase transition should not be expected to occur. However, the results obtained by T evolution between 298 K and 140 K (cooling and heating rates of 1.0 and 0.5 K·min^{-1}, respectively) as shown in Figures 1B and 1C argue strongly against this expectation.

Cooling Process. The peaks of ν_{1OH} and ν_{3OH} monotonously shifted to lower wavenumber regions (Figure 1B), which could be explained by the relationship between T and the O−H stretching fundamentals and that of the HB force. On the other hand, the absorbance change was not linear: it was maximum at ~260 K and then decreased (Figure 1C top, A_X: the subscript, X, indicates the peak position at 298 K.). The increment, but not the decrement, can be explained by the relationship between absorptivity and the HB force. Concomitantly with the decrement, a new band in a region of 3500–3100 cm^{-1} appeared (Figures 1B and 1D). This indicates that monomolecular water is converted to an associated state (cluster) below ~260 K. Furthermore, below ~238 K, a new well-defined peak appeared around 3280 cm^{-1} and the value of A_{3280} dramatically increased (Figure 1C bottom). The magnified spectra (Figure 1D) of the sorbed water in the regions from ~260 to ~238 K and below ~238 K are similar to those of supercooled water and ice I$_h$, respectively. (The spectrum for supercooled water at 241 K could not be measured. Therefore, the spectrum of ice I$_h$ at 241 K is shown in the figure.) These results clearly show the phase transition of the so-called NFB water: condensation below ~260 K and freezing at ~238 K. Furthermore, it was not only the ordinary phase transition from liquid to solid but also included a vapor deposition process. There are two pieces of evidence for vapor deposition: (1) A_{3280}, in the case of ice I$_h$, increased linearly (Figure 2), whereas in the present case it did not: the rate of increment in A_{3280} of ~190% from 235 K to 200 K was much larger than that for ice I$_h$ (~10%). (2) The slope of the A_{3670} increased below ~238 K, indicating acceleration of the decrement in monomolecular water. The increment corresponds to the fact that the vapor pressure of water on the plane surface of liquid water is larger than that of ice.

Heating Process. The changes were not the same as the cooling process. The characteristic difference in the *spectral profile* was seen in the region from ~240 K to ~268 K (Figure 1B). On the other hand, a difference in the region from 140 K to ~240 K was not observed. The spectrum of the sorbed water is similar to that of ice I$_h$ at a corresponding T up to ~268 K (Figure 1D bottom). This indicates that the liquid water observed above ~240 K in the cooling process is merely in the supercooled state and is not so-called FB water that cannot freeze at the thermodynamic melting point by hydration. This is connected to the thermodynamic hysteresis normally observed during a phase transition. In this process, the frozen sorbed water did not only melt but also sublimed. As mentioned above, this is supported by no observation of the liquid-like spectrum below 268 K. Furthermore, a synchronous acceleration of a decrease in A_{3280} and an increase in A_{3671} at ~208 K also suggested sublimation (Figure 1C). It is not clear at present why sublimation occurs at ~208 K.

The findings described here require reconsideration of the general understanding of water in a very weakly hydrated polymer system. The occurrence of vapor deposition and sublimation has a very important meaning for calorimetric analysis. This is because the amounts (ratios) of free, FB, and NFB water are calculated on the basis of the assumption that the thermal response around 273 K corresponds to the freezing/melting of water.

Supporting Information Available: an experimental method. This information is available free of charge via the Internet at http//pubs.acs.org.

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Figure Caption

Figure 1. Infrared spectra of sorbed water into solid polystyrene. (A) Sorbed water in the case of water content of 0.3 wt% at 298 K. Dotted line: ice I_h at 140 K; broken line: liquid water at 298 K; broken-dotted line: water vapor at 298 K. (B) Spectra in a T region of 298 K – 140 K. left: cooling; right: heating. (Corresponding contour map is shown in Table of Contents (TOC)). (C) Temperature-dependence of peak absorbance for A_{3671} and A_{3280}. The A_{3280} value corresponds to the absorbance at a peak around 3280 cm^{-1} in the regions below 238 K on cooling and below 266 K on heating, and to the absorbance at 3280 cm^{-1} in other T regions. (D) Magnified spectra. Dotted line: supercooled water (262 and 250 K on cooling and 270 K on heating) and ice I_h.

Figure 2. Infrared spectra of pure water at various temperatures. (A) Cooling (left) and heating (right) processes. (B) Temperature-dependence of peak absorbance for A_{3280}.
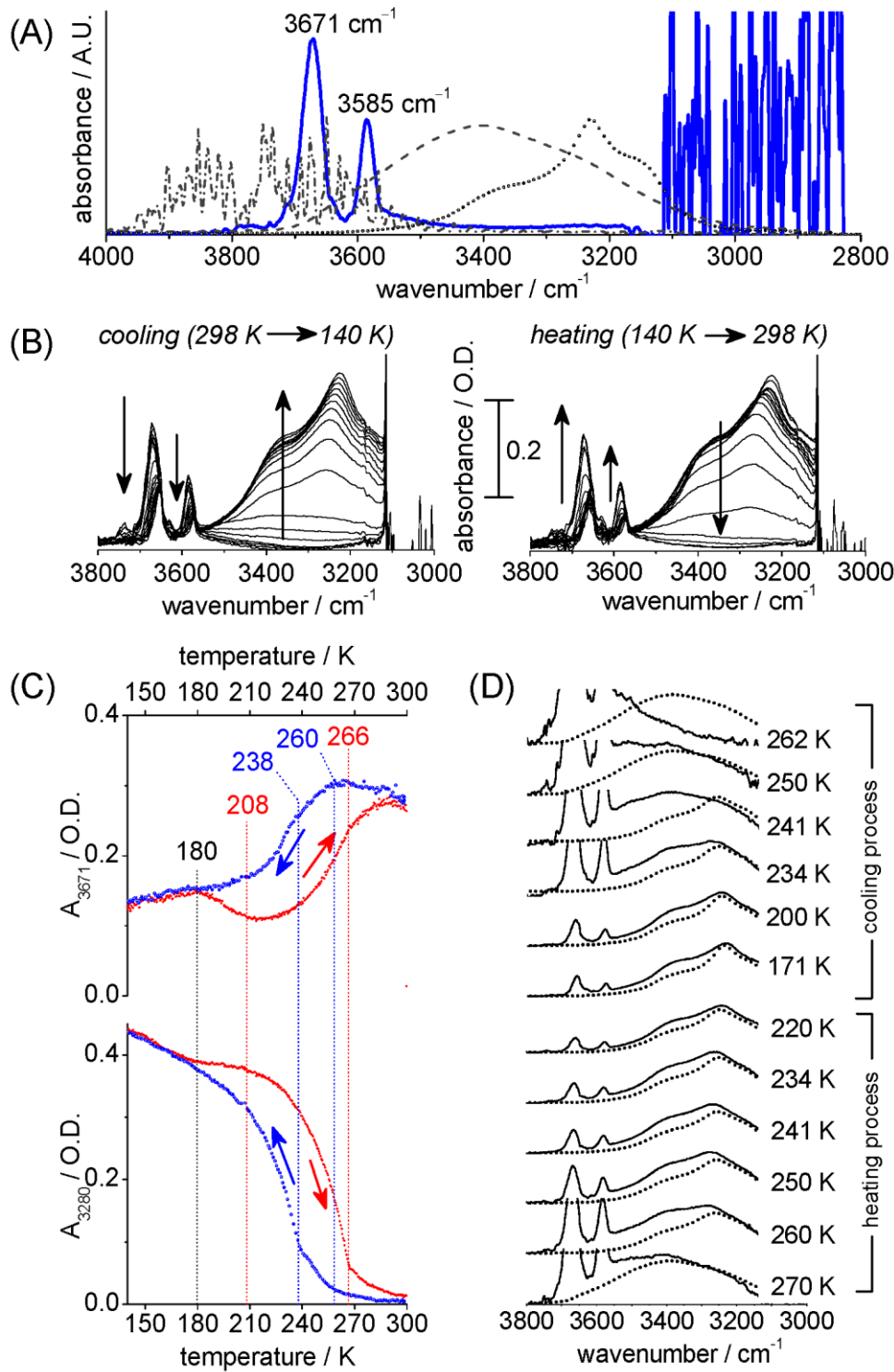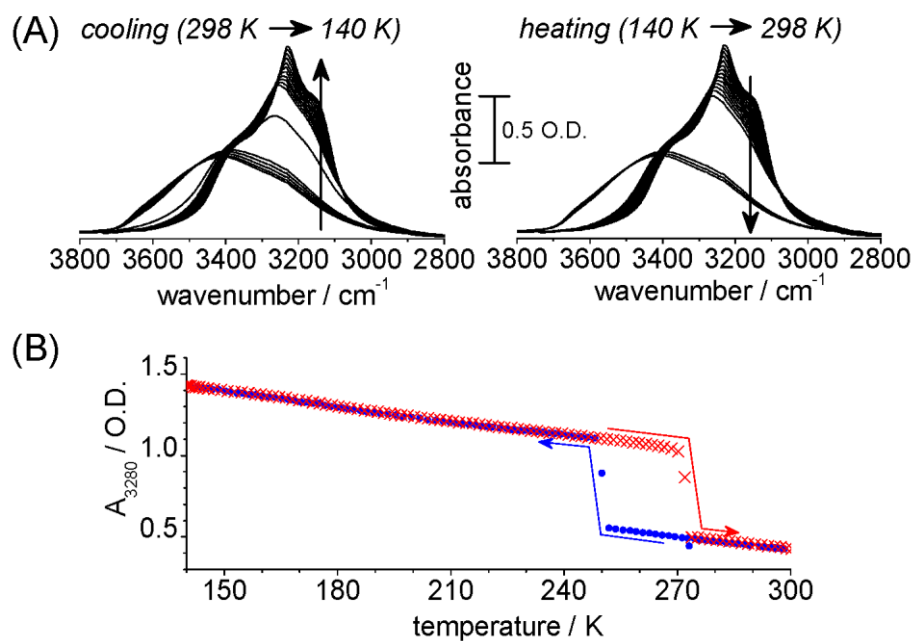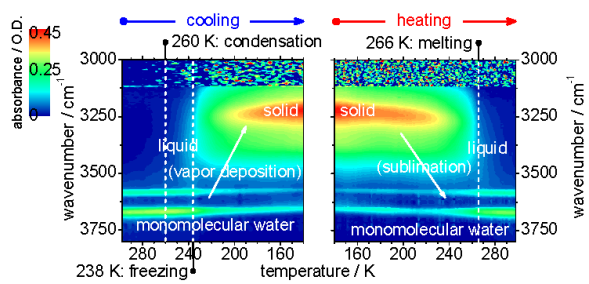
Figure 1. Gemmei-Ide & Kitano.

Figure 2. Gemmei-Ide & Kitano.

TOC Image

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