**Crystal Growth of Ice I_h by Re-vapor-deposition and Diffusion Suppression of
Monomolecular Water in a Polymer Solid:
Spectroscopic Observation of Phase Transition of Water
Sorbed into Solid Polystyrene**

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Abstract Monomolecular water in a solid polymer, which has no effective hydrogen bonding sites, was revealed by temperature-variable Fourier transform infrared spectroscopy to be condensable and crystallizable. Ice I_h formed in the polymer matrix was grown by vapor deposition and was reduced by sublimation. Moreover, rapid cooling induced crystal growth by vapor deposition during *heating (re-vapor-deposition)*. These results indicate the requirement of a change in the generally accepted understanding of the thermal responses of water in a polymer matrix and give rise to a problem for general interpretation of the category of water in a polymer matrix based on calorimetric analysis at very low water contents.

Key Words

Phase Transition / Monomolecular Water / Polymer Solid / IR Spectroscopy

Introduction

Solidification processes of molecular fluid are classified into vapor deposition, crystallization and vitrification (glass formation). The former two processes are governed by the chemical potential. Vitrification, on the other hand, is not “transition” in the thermodynamic sense of the word and is strongly related to cooling rate: glass is not formed if the cooling is not sufficiently fast in comparison with the crystallization.

Vapor deposition and vitrification occur only during cooling, but crystallization occurs during both cooling and heating. Crystallization during heating is called “recrystallization” and is a transformation from glass to crystal state or from glass to supercooled liquid and subsequently to crystal state. Vapor deposition and vitrification in a heating process have not been reported in the literature.

Water is one of the most extensively investigated materials. Its thermodynamic melting, homogeneous nucleation, and recrystallization (of hyperquenched amorphous solid water) temperatures are 273 K, 236 K,¹ and ~150 K,² respectively, and its vitrification temperature (T_g) is assigned in the range of 120–160 K.³ All of the four temperatures are changed by the existence of a solute: the former two T s and the others tend to be depressed and raised, respectively.^{2,4} Polymers that are soluble in water as a solute also change the three transition T s and T_g . In a high concentration region (several ten weight percent), none of the three transitions are observed. Water in such a system is called “non-freezable bound water” (NFB water).⁴ In a higher concentration region, i.e., extremely low water content (subpercent level), water is no longer regarded as a “solvent” but rather as a “sorbate”. In such conditions, needless to say, water is speculated to exist as NFB water. A reason for the speculation is that, even if phase transition occurs, the most frequently used apparatus, a differential scanning calorimeter (DSC) cannot detect it due to extremely low water content, i.e., extremely small heat flow with it.

In this study, whether an extremely small amount of water in a solid polymer without effective hydrogen bonding (HB) sites phase-transforms was examined by temperature-variable Fourier transform infrared (IR) spectroscopy. IR spectroscopy cannot detect a heat flow with the phase transition but has two significant advantages: (1) a very high sensitivity for water and (2) in situ measurement of the state of water without any perturbations.

Temperature dependence on cooling of an IR spectrum for water in a solid polystyrene (water content = ~0.026 wt%) indicated the existence of phase transition of water from monomolecular to liquid and subsequently to a solid state. These phase transitions were only “condensation” and “crystallization”, respectively. Ice I_h , however, once formed in the solid polystyrene was grown by vapor deposition during cooling and was reduced by sublimation during heating. These results

indicate the requirement of a change in the widely accepted understanding for the thermal response of monomolecular water in polymer solids (at least in the case of a polymer without an effective HB site). Furthermore, rapid cooling induced not only prevention of the growth of ice I_h during cooling but also the growth of ice I_h by vapor deposition during heating (re-vapor-deposition). Such a solidification phenomenon via vapor deposition during heating has not been reported in the literature.

Experiments

Polymer Solid. Atactic polystyrene (PSt) with $M_w = 9.0 \times 10^5$ ($M_w/M_n = 1.4$) (WAKO, Japan) was purified by precipitation in chloroform–ether. A pellet of the PSt with a diameter of ~ 13 mm and a thickness of ~ 1700 μm was prepared from a spectroscopic-grade toluene solution of $5 \text{ g} \cdot \text{L}^{-1}$ on one side of a sapphire substrate and a thermal treatment was carried out. The pellet was hydrated under humid air with a constant relative humidity of 53% for 2 weeks at 298 K. The hydrated sample was set in a homemade sample-holder and then tightly sealed with indium. The water content of the hydrated sample was determined to be ~ 0.026 wt% by Karl Fischer's method.

Infrared Spectroscopy. IR spectra for the hydrated and the dried samples were recorded on a Spectrum One NTS (Perkin-Elmer) with a resolution of 4 cm^{-1} and a scanning time of 20 s. Cooling rates were 0.5 and $5.0 \text{ K} \cdot \text{min}^{-1}$ and heating rate was $0.5 \text{ K} \cdot \text{min}^{-1}$. Sample temperature was controlled by an Optistate-DN cryostat (Oxford) connected to a model ITC601 temperature controller. IR spectra for the water sorbed into the solid PSt were obtained by subtraction between the spectra of the hydrated and the dried samples at the same T .

Results and Discussion

State of Sorbed Water. Figure 1 shows a spectrum of water sorbed into the solid PSt at 298 K together with spectra for water vapor, liquid water and ice I_h (at 140 K). The sorbed water had only two sharp peaks at 3671 and 3585 cm^{-1} , which were assigned to symmetric ($\nu_{1\text{OH}}$) and anti-symmetric ($\nu_{3\text{OH}}$) OH stretching fundamentals.⁵ The fringe-like patterns around 3765 and 3657 cm^{-1} , which were $\nu_{1\text{OH}}$ and $\nu_{3\text{OH}}$, respectively, of water vapor disappeared, and both the fundamentals shifted to a lower wavenumber. This indicates the restriction of sorbed water by a weak electrostatic interaction between water molecules and π -electrons of a phenyl ring.⁶ Furthermore, the large difference from liquid water clearly indicates that the sorbed water does not form associated water. These spectral characteristics show that the sorbed water is restricted monomolecularly on phenyl ring.

Ordinal Phase Transition. Figure 2 shows T dependence of the spectra of sorbed water. Both rates of cooling and heating were $0.5 \text{ K} \cdot \text{min}^{-1}$.

In the cooling process (panel A), the peaks of $\nu_{1\text{OH}}$ and $\nu_{3\text{OH}}$ of the sorbed water monotonously shifted to lower wavenumber regions, which could be explained by the relationship between T and the OH stretching fundamentals and that of the electrostatic interaction. The absorbance change, on the other hand, was not linear: it was maximum at ~ 267 K and then decreased (panel C, A_X : the subscript, X, indicating peak position at 298 K). The A_{3280} value corresponds to the absorbance at a peak around 3280 cm^{-1} in the regions below 240 K on cooling and below 270 K on heating, and to the absorbance at 3280 cm^{-1} in other T regions. The increment, but not the decrement, can be explained by the relationship between absorptivity and the electrostatic interaction. Concomitantly with the decrement, a new broad component in a region of $3500\text{--}3100 \text{ cm}^{-1}$ appeared. This indicates that monomolecular water is converted to an associated state below ~ 267 K. Furthermore, below ~ 240 K, a new well-defined peak appeared around 3280 cm^{-1} (panel A) and the value of A_{3280} dramatically increased (panel C). The magnified spectra (panel A bottom) in the regions from ~ 267 to ~ 240 K and below ~ 240 K are similar to those of supercooled water and ice I_h , respectively. These results show the phase transition of the monomolecular water: condensation below ~ 267 K and crystallization at ~ 240 K.

In the heating process (panel B), the changes were not the same as those in the cooling process. The characteristic difference in the spectral profile was seen in the region from ~ 240 K to ~ 270 K. The spectrum of the sorbed water is similar to that of ice I_h at a corresponding T up to ~ 270 K (panel B 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 non-freezable bound water⁴ that cannot freeze at the thermodynamic melting point by hydration. The difference from the cooling process should be thermodynamic hysteresis normally observed during a phase transition. In this process, the crystallized sorbed water melted at 270 K and then vaporized.

The monomolecular water sorbed into solid PSt could be condensed and then crystallized at ~ 240 K, and it melted at ~ 270 K and then vaporized during heating. Condensable monomolecular water, however, was not all of the sorbed water because the two peaks assigned to monomolecular water existed in all T regions.

Vapor Deposition and Sublimation. Figure 2C shows crystal growth of ice I_h by vapor deposition during cooling and reduction of Ice I_h by sublimation during heating. The value of dA_X indicates the rate of change in A_X per 1 K. As shown in Figure 3C, the change in the value of A_{3280} for normal water at liquid-to-solid and solid-to-liquid phase transitions was very large and discontinuous. On the other hand, the change for the PSt system was different from this.

Three pieces of evidence for vapor deposition are as follows: (1) the value of dA_{3280} in the case of ice I_h was constant at $\sim 0.2 \times 10^{-2} \text{ K}^{-1}$ (Figure 3C), whereas it was not constant in the present case. (2) The values of dA_{3671} and dA_{3280} became more negative and positive at ~ 240 K, respectively, and below 240 K the value of dA_{3280} was much larger than that for ice I_h . These changes indicate accelerations of the decrement in monomolecular water and the crystal growth. This corresponds to the fact that the vapor pressure of water on the plane surface of liquid water is larger than that of ice. (3) No liquid-like spectrum was observed below ~ 240 K. This vapor deposition might exist above ~ 180 K, in other words, not

below ~ 180 K. This is because the value of dA_{3280} below ~ 180 K in the present case is comparable to that for ice I_h . In the same logic, there are three pieces of evidence for sublimation: (1) a much larger value of dA_{3280} above 216 K than that for ice I_h , (2) a synchronism of changes in dA_{3671} and dA_{3280} at ~ 216 K, and (3) no observation of a liquid-like spectrum below ~ 270 K. This sublimation might onset at ~ 216 K because the value of dA_{3280} in the present case was comparable to that for ice I_h below ~ 216 K.

Vapor deposition and sublimation of water in the PSt matrix exist in the T region from ~ 240 K to ~ 180 K during cooling and in the T region from ~ 216 K to ~ 270 K during heating, respectively. This vapor deposition might be a diffusion-controlled process because this phenomenon should be required for the dissociation of monomolecular water from the polymer chain (i.e., diffusion in the matrix). If this is correct, a rapid cooling should prevent the crystal growth.

Re-vapor-deposition. Figure 4 shows the T dependence of the spectra of sorbed water when cooling and heating rates were 5 and $0.5 \text{ K} \cdot \text{min}^{-1}$, respectively. The difference in the conditions from those for Figure 2 was only the cooling rate.

In the cooling process (panel A), the sorbed water was condensed again and then crystallized at ~ 240 K as was the case when the cooling rate was $0.5 \text{ K} \cdot \text{min}^{-1}$. This interpretation is based on the same reason as that mentioned above. On the other hand, the values of A_{3671} and A_{3280} were larger and smaller than those in Figure 2, respectively, in all T regions (panels A, C; intensity scale is the same as that in Figure 2). Although there is no noticeable difference except for this point, this strongly supports the diffusion-controlled process of crystal growth.

In the heating process (panel B), in stark contrast to the cooling process, a notable difference from Figure 2B was observed: as seen in the contour map (panel B middle), the crystal growth of ice I_h occurred again during heating. It began at ~ 180 K and became maximum at ~ 220 K (panel C bottom). Such a crystal growth in the heating process, i.e., so-called “recrystallization” of water, has been reported in some (but not many) systems.⁷ In most cases, the recrystallization of water has been observed in concentrated aqueous solutions. The general explanation for it is that vitreous water (glassy water), which might be formed by rapid cooling, crystallizes during heating. In the present case, however, this explanation can hardly be adapted because of a synchronism of an increase in A_{3280} (crystal growth) with a decrease in A_{3671} (decrease of monomolecular water) (panel C) at ~ 180 K. The synchronism indicates crystal growth by the deposition of monomolecular water. Vapor deposition during heating, as far as we know, has not been reported previously in the literature. We propose that this phenomenon be called “*re-vapor-deposition*” in imitation of the term “recrystallization”. This is to avoid confusion with the term “*vapor redeposition*” frequently used in the field of solid surface processing via vapor deposition.

Diffusion Suppression of Monomolecular Water. The re-vapor-deposition began at ~ 180 K as mentioned above (Figure 4). A plausible reason why the re-vapor-deposition began at this T is that below this T the diffusion of monomolecular water is suppressed, i.e., the monomolecular water drops into the glassy state in a broad sense (of course, assisted by the PSt chain). At present, there is no direct evidence for divergence of the diffusion coefficient for monomolecular water. Four pieces of indirect evidence, however, can be seen in panel C in Figures 2 and 4: (1) no thermal hysteresis of A_{3671} and A_{3280} below ~ 180 K, (2) in the cooling process, relaxations for changes in A_{3671} and A_{3280} around 220 K and subsequent linear relations between the two absorbances and T below ~ 180 K, (3) no relations of (1) and (2) with cooling rate, and (4) in the heating process, the occurrence of re-vapor-deposition at ~ 180 K. These four experimental results can be explained by the diffusion suppression of monomolecular water. This dynamic crossover from fluid to a glass-like state or vice versa might correspond to a balancing point between the dissociation force by the diffusion and the restriction force by the electrostatic interaction.

Conclusions

Water monomolecularly sorbed into a polymer solid, which has no effective HB sites, was revealed for the first time to be condensable and crystallizable. These phenomena might not be strange if the polymer matrix is regarded to be only assemblies of very small holed cages (bottles) confining water vapor. However this cage, i.e., the polymer chain, sterically and physically (due to a weak electrostatic interaction) inhibits the diffusion of water molecule and induces the prevention of condensation and crystal growth of ice I_h during cooling and the generation of recrystallization during heating when cooling is rapid. On the other hand, these phenomena cannot be said to be general. In the case of polymethylmethacrylate (PMMA) having a T_g , 383 K, comparable with that of PSt (370 K) but ester and ether groups as effective HB sites, condensation (of course, also crystallization) was not observed even when the water content of PMMA was ten times more than that of PSt.⁸ On the other hand, in the case of poly(*n*-butylacrylate) (PBA) having an ester group as an effective HB site but very low T_g , 220 K, at the same hydration level as that in the present case, both condensation and crystallization of water (including vapor deposition and sublimation of ice I_h) were observed, but recrystallization (re-vapor-deposition) was not observed.⁹ The differences between the three systems (PSt, PMMA, and PBA) indicate that two important points for the phenomena observed in the case of PSt might be (1) the polymer chain does not have an effective HB site and (2) movement of the polymer chain as a cage is frozen (i.e., T_g of PSt, 370 K, is much higher than the experimental temperature, 298–140 K).

The occurrence of growth/reduction of ice I_h by vapor deposition/sublimation and recrystallization by vapor deposition (re-vapor-deposition) has a very important meaning and gives rise to a problem for the general understanding of the thermal response of water in polymer solids in the low water content region. The general understanding based on calorimetric analysis is that, without relation to the water content, a DSC signal in the sub-zero temperature region, 240–273 K, is assigned to the melting or crystallization of water. The present results, however, strongly deny this and

indicate the need to change this understanding at least with regard to low water content.

Acknowledgement This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 20750175) from Ministry of Education, Culture, Sports, Science and Technology of Japan, and a Grant-in-Aid for Scientific Research (B) (No. 19350055) from the Japan Society for the Promotion of Science.

References and Notes

- 1) See, for example: (a) Hobbs, P. V. *Ice Physics*; Clarendon Press: Oxford, U.K., 1974; pp 461–523. (b) Angell, C. A. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1982; Vol. 7, pp 1–81.
- 2) Hofer, K.; Mayer, E.; Johari, G. P. *J. Phys. Chem.* **1991**, *95*, 7100.
- 3) Angell, C. A. *Science* **2008**, *319*, 582.
- 4) Jhon, M. S.; Andrade, J. D. *J. Biomed. Mater. Res.* **1973**, *7*, 509.
- 5) Kusanagi, H.; Yukawa, S. *Polymer* **1994**, *35*, 5637.
- 6) Gruenloh, C. J.; Carney J. R.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Jordan, K. D. *Science* **1997**, *276*, 1678.
- 7) Franks, F. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1982; Vol. 7, Chapter 3.
- 8) Gemmei-Ide, M.; Motonaga, T.; Kitano, H. *J. Phys. Chem. B* **2007**, *111*, 5533.
- 9) To be submitted.

Figure Captions

Figure 1. Infrared spectra of water sorbed into solid polystyrene at 298 K. Solid line, sorbed water; broken line, liquid water; broken-dotted line, water vapor; dotted line, ice I_h at 140 K.

Figure 2. Temperature-dependence of the spectra of sorbed water at cooling and heating rates of $0.5 \text{ K} \cdot \text{min}^{-1}$. (A) Cooling. (B) Heating. (C) T -dependence of A_X and dA_X . Right, cooling; left, heating.

Figure 3. Temperature-dependence of the spectra of pure water at cooling and heating rates of $0.5 \text{ K} \cdot \text{min}^{-1}$. (A) Cooling. (B) Heating. (C) T -dependence of A_{3280} and dA_{3280} . Right, cooling; left, heating.

Figure 4. Temperature-dependence of the spectra of sorbed water at a cooling rate of $5 \text{ K} \cdot \text{min}^{-1}$ and at a heating rate of $0.5 \text{ K} \cdot \text{min}^{-1}$. (A) Cooling. (B) Heating. (C) T -dependence of A_X and dA_X values. Right, cooling; left, heating.

Figure 1. Gemmei-Ide & Kitano

Figure 2. Gemmei-Ide & Kitano

Figure 3. Gemmei-Ide & Kitano

Figure 4. Gemmei-Ide & Kitano