

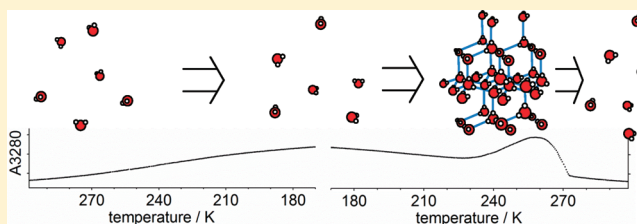
Recrystallization of Water in Non-Water-Soluble (Meth)Acrylate Polymers Is Not Rare and Is Not Devitrification

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S Supporting Information

ABSTRACT: Change in the state of water sorbed into four kinds of non-water-soluble poly(meth)acrylates with low water content by temperature (T) perturbation was examined on the basis of T variable mid-infrared (MIR) spectroscopy. Many studies using differential scanning calorimetry suggested that there was no change in the state. T dependence of their MIR spectra, however, clearly demonstrated various changes in the state. Furthermore, recrystallization, which was crystallization during heating, was observed in all four polymers. The recrystallization observed in this study was not devitrification, which is the change in the state from glassy water to crystalline water, but vapor deposition during heating (vapor re-deposition). There were only two reports about recrystallization of water in a non-water-soluble polymer before this report; therefore, it might be considered to be a rare phenomenon. However, as demonstrated in this study, it is not a rare phenomenon. Recrystallization (vapor re-deposition) of water in the polymer matrices is related to a balance between flexibility and strength of the electrostatic interaction sites of polymer matrices but might not be related to the biocompatibility of polymers.



■ INTRODUCTION

Various synthetic polymers have been used as base or coating materials for biomedical devices such as contact lenses, vascular grafts, heart-lung machines, and artificial kidneys. The ability of surfaces to prevent protein adsorption and cell adhesion, that is, biocompatibility, is required for such applications of synthetic polymers. The biocompatibility is known to depend on charge, wettability, free energy, roughness, and stiffness of the polymer surface, but a universal explanation for the origin of it has not yet been obtained.^{1–5} Polymers and biological components have infinite variations in their chemical structures. Water, on the other hand, is the only common substance when biocompatibility is investigated; therefore, the physicochemical property of water (water structure) is expected to play a crucial role in biocompatibility.

The results of some studies on the relation of biocompatibility to water structure in aqueous polymer solutions^{6–9} and non-water-soluble polymers^{10–22} have been reported. Among them, the water structure in poly(2-methoxyethyl acrylate) (pMEA), which is a non-water-soluble polymer and a polymer with high blood compatibility, has been examined by differential scanning calorimetry (DSC),^{10–16} X-ray diffraction spectroscopy,¹⁷ nuclear magnetic resonance spectroscopy,¹⁸ and mid-infrared (MIR) spectroscopy.^{19–22} On the basis of results of DSC analysis, it was proposed that biocompatible polymers have “intermediate water” (cold-crystallizable water, recrystallized water, or freezing bound water).^{10–16} “Intermediate water” was defined as water that is frozen (crystallized) only during heating. In the general definition in DSC, however,

“intermediate water” is water that is frozen or molten at a lower temperature (T) than the thermodynamic melting T (T_m) of water, 273 K,²³ regardless of the direction of T change. To avoid confusion in this report, the term “recrystallized water” is used.

There have been some reports based on DSC analysis about recrystallized water in aqueous polymer solutions.^{24–28} Recrystallization of water is generally considered to be devitrification that glassy water crystallizes during heating. In the case of non-water-soluble polymers, on the other hand, there have been only two cases of pMEA¹⁰ and poly-(tetrahydrofurfuryl acrylate) (pTHFA),¹⁴ as far as we know. pTHFA is also a polymer with high blood compatibility. It was thought that recrystallized water in the two polymers also originated from glassy water and was in a condensed state, which had a special structure to avoid protein adsorption, at physiological T .^{10–16}

It is not clear whether the recrystallized water is a necessary and sufficient condition for biocompatibility, and the aim of this study was not to verify that recrystallized water induces biocompatibility. Clarification of the correlation of water structure to the biocompatibility of polymers was also not the aim. The aim of this study was to determine whether recrystallization of water in non-water-soluble polymers is physicochemically the same as that in aqueous polymer

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Table 1. Characteristics of Polymers Used

	polymer							
	pMA ^a	pBMA ^a	pEEA ^a	pEEMA ^a	pMMA ^b	pBA ^c	pMEA ^d	PS ^e
$M_w \times 10^3$ (M_w/M_n)	77 (1.9)	54 (1.8)	75 (4.8)	61 (4.4)	900 (1.4)	79 (1.5)	86 (1.7)	900 (1.4)
water content (wt %)	1.83	0.20	2.42	1.23	5.48	0.44	3.20	0.026
T_g (K)	280 ^f	288 ^g	223 ^h	257 ⁱ	412 ^g	219 ^j	223 ^k	373 ^l
density (g·cm ⁻³)	1.21 ^f	1.07 ^g	(1.11) ^m	1.11 ⁱ	1.19 ^g	1.06 ^j	(1.11) ^m	1.04 ^l
number of O atoms (mol·cm ⁻³)	0.0281	0.0148	0.0231	0.0211	0.0236	0.0165	0.0256	

^aThis work. ^bReference 30. ^cReference 47. ^dReference 48. ^eReference 29. ^fReference 51. ^gReference 52. ^hReference 56. ⁱReference 53. ^jReference 54. ^kReference 10. ^lReference 55. ^mThe values were not obtained in the literature. Therefore, the values are assumed to be the same as that of pEEMA.

solutions, that is, devitrification. This is because, if the consideration about pMEA and pTHFA is correct, it means that the formation of glassy water is achieved by a very slow cooling of 2.5 K·min⁻¹. Under ambient pressure, the preparation of glassy water generally requires rapid cooling (quenching) of the system, and there have, therefore, been no reports of preparation of glassy water without quenching. In the present study, four kinds of poly(meth)acrylates having recrystallized water were newly discovered spectroscopically, and on the basis of investigation of change in the state of the sorbed water by T variable MIR spectroscopy, it was examined whether recrystallization of water in non-water-soluble polymers is devitrification or not. The four poly(meth)acrylates examined were poly(methyl acrylate) (pMA), poly(*n*-butyl methacrylate) (pBMA), poly(ethoxyethyl acrylate) (pEEA), and poly(ethoxyethyl methacrylate) (pEEMA). The differences in the chemical structure are as follows: (1) the two latter ones (pEEA and pEEMA) have an ether group in the side chain as the same as pMEA, whereas the two former ones do not; (2) pBMA and pEEMA have an α -methyl group in the main chain, whereas pMA and pEEA do not. There have been no reports that the four polymers are biocompatible materials.

Before beginning the results and discussion, mention should be made here of several terms used in this report. The terms “condensation”, “vaporization”, “vapor deposition”, “sublimation”, and “vapor re-deposition” were used for expressing the change in the state of the sorbed water in the polymer matrix. From the point of view of physical chemistry, these five terms would not be suitable because monomeric water in the polymer matrix should not be in a gas state but associated with polymer chains via electrostatic interaction. However, if the polymer chains are omitted, the change in the state from/to monomeric to/from condensed state might be able to be regarded as the above expressions. The term “crystallization” is generally used for the change from liquid water to crystalline water. In this report, however, it was used for the formation of ice regardless of its process. Instead of this, the term “freezing” was used for the change from liquid water to ice.

EXPERIMENTS

Poly(methyl acrylate) (pMA), poly(*n*-butyl methacrylate) (pBMA), poly(2-ethoxyethyl acrylate) (pEEA), and poly(2-ethoxyethyl methacrylate) (pEEMA) were prepared by a conventional free radical polymerization of corresponding monomers in toluene at 350 K using 2,2'-azobisisobutyronitrile as a thermal initiator. Their weight-averaged molecular weights (M_w) and polydispersity indices (M_w/M_n) determined by gel permeation chromatography are given in Table 1. Measurement of T dependence of the MIR spectrum of sorbed water has been described.^{29,30} Briefly, the sample, which was prepared as a film on a sapphire substrate of 13 mm in diameter by a

solvent-cast method, was hydrated by exposing it to humid air with 88% relative humidity at 310 K for 10 days. The water content of hydrated samples in weight percent was determined by the Karl Fischer method (Table 1). The sample was set in a homemade sample-holder and then tightly sealed with indium so that the water content was constant during the measurement. MIR spectra of the hydrated and 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 in a temperature (T) range from 298 to 170 K. Cooling and heating rates were 0.5 K·min⁻¹. The temperature of the sample (T) was controlled by an Optistat-DN cryostat (Oxford) connected to a model ITC601 T controller. The spectra of the sorbed water were obtained by subtraction between the spectra of the hydrated and dried samples at the same T .

RESULTS

Spectrum at 298 K (Figure 1). MIR spectra of water sorbed into the four polymers and the spectrum of pure water

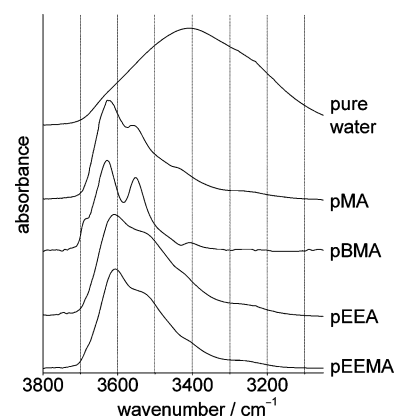


Figure 1. MIR spectra of water sorbed into the four (meth)acrylate polymers and pure water at 298 K.

at 298 K are given in Figure 1. Pure water has a broad main peak centered at ~ 3400 cm⁻¹ and two shoulders at 3630 and 3280 cm⁻¹ in its MIR spectrum. The higher frequency shoulder is attributed to three-coordinate asymmetrically hydrogen (H)-bonded water molecules.^{31,32} The lower frequency shoulder is generally attributed to the symmetric OH stretching mode (ν_{OH}) of tetrahedrally coordinated water molecules (strongly H-bonded water molecules), and the main peak is attributed to the ν_{OH} of asymmetrically H-bonded water molecules.^{31,32} On the other hand, the spectra of water sorbed into the four kinds of polymers are very different from the spectrum of pure water, suggesting that most of the sorbed water is associated with electrostatic interaction sites of the polymers and is not in the

liquid state. In the higher frequency region over 3500 cm^{-1} , two bands at ~ 3615 and $\sim 3540\text{ cm}^{-1}$ and an obscured shoulder at $\sim 3690\text{ cm}^{-1}$ are observed.

Recently, Iwamoto³³ and Iwamoto et al.³⁴ reported MIR spectra of 1:1 and 1:2 complexes between a water molecule and di-*n*-butyl ether, 3-decanone, or methyl decanoate in *n*-heptane and proposed band assignments for the three components mentioned above. Band assignments were made according to them in this report. Water molecules in the polymer matrix should be bonded to the electrostatic interaction sites with both of their H atoms or with one of their H atoms. The former and the latter are denoted as “bridging water” and “dangling water”, respectively. The high frequency shoulder at $\sim 3690\text{ cm}^{-1}$ is attributed to the stretching mode of the non-H-bonded OH group of dangling water. The high frequency band at $\sim 3615\text{ cm}^{-1}$ is attributed to the asymmetric OH stretching mode of the bridging water. The low frequency band at $\sim 3540\text{ cm}^{-1}$ has two origins: (1) stretching mode of the H-bonded OH group of dangling water and (2) symmetric OH stretching mode of bridging water. The intensive band from bridging water and the weak band from dangling water indicate that most of the sorbed water is bridging water.

In the case of pMA, pEEA, and pEEMA, two small shoulders were observed at ~ 3450 and $\sim 3250\text{ cm}^{-1}$. As stated above, the two bands in this low frequency region are generally considered to be weakly and strongly H-bonded water molecules (between liquid water molecules). At present, it is unclear whether this water is liquid water or a small water cluster. The amount of this water, however, should be small because the absorption coefficient is strongly enhanced by fully H-bonding formation.³⁵

After all, most of the sorbed water in the four polymers was found to be the bridging water. The higher frequency band at $\sim 3615\text{ cm}^{-1}$ rising from the bridging water is well isolated from the spectrum of pure water. This band intensity is used as an indicator of the change in the amount of the bridging water, that is, the monomolecular water isolated in the polymer matrix.

Spectral Changes by T . Figures 2, 3, and 4 show T dependence of the MIR spectrum of pure water and the spectra of water sorbed into pBMA and pEEMA, respectively. The results for pMA and pEEA are given in Figures S1 and S2, respectively, in the Supporting Information because they are similar to those of pBMA or pEEMA. The right and left panels for each figure show the results at cooling and heating, respectively. Panel a shows the original spectra selected at every $\sim 10\text{ K}$ from 298 to 170 K. Panel b shows T dependence of a peak absorbance assigned to the bridging water (A_{xxxx} , top) and that of a peak absorbance at $\sim 3280\text{ cm}^{-1}$ (A_{3280} , bottom). Arabic number “xxxx” of A_{xxxx} corresponds to a peak position of the bridging water at 298 K. In the text, “Axxxx” is denoted as “ A_{MONO} ”. Vertical lines in panel b indicate maximal, minimal, or bending points of A_{MONO} or A_{3280} . Arabic numbers on the vertical line are their T 's. CX or HX (X: arabic number) is a numbering for T range divided by the lines. Panel c shows the difference spectra between two original spectra at both side T 's in each T range. CX or HX on the left top side of each spectrum corresponds to that in panel b. If jump-up/-down of A_{3280} was observed, the numbering in panel b was placed on the vertical line and the difference spectrum in panel c was calculated from the two original spectra at $\pm 1\text{ K}$ of the jump point.

The values of A_{3280} and A_{MONO} were the presented peak intensity of the IR spectra without a band resolution (for example, the Gaussian deconvolution). The component

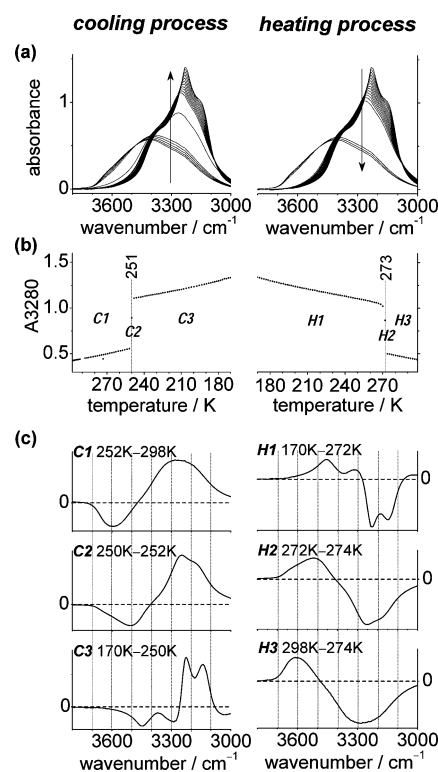


Figure 2. T dependence of the MIR spectrum of pure water: (a) original spectra at every $\sim 10\text{ K}$ from 298 to 170 K; (b) T dependence of A_{3280} ; (c) difference spectra in each T range.

assigned to the bridging water was also overlapped with the other component assigned to the dangling water; therefore, the change in the value of A_{MONO} was not equal to the change in the amount of the bridging water. However, the value of A_{MONO} should be used as an indicator of the change in the amount of the monomolecular water, because both the bridging water and the dangling water are the monomolecular water isolated in the polymer matrix and the IR component of the bridging water was separated from that of liquid water. On the other hand, the value of A_{3280} might have a double origin (the small water cluster and liquid water (ice)); therefore, the value of A_{3280} cannot directly give the exact amount of liquid water (ice). However, as seen in the case of pure water (Figure 2), the ice formation can be decided from the discontinuous change in the value of A_{3280} and the spectral profile.

A. Pure Water (Figure 2). By cooling, MIR spectra of pure water with a very broad feature above 251 K changed promptly to those with a sharp band at $\sim 3280\text{ cm}^{-1}$ (panel a). Oppositely, by heating, the sharp band returned to the broad one above 273 K . The two changes are freezing and melting, respectively. The sharp peak at $\sim 3280\text{ cm}^{-1}$ in the lower T side characterized ice I_h , but before freezing (after melting), only a shoulder was observed. If there was no clear peak at $\sim 3280\text{ cm}^{-1}$, the value of A_{3280} was adapted to an absorbance fixed at 3280 cm^{-1} . This rule was also applied to the case of sorbed water. Jump-up and -down of A_{3280} were observed at 251 and 273 K in cooling and heating, respectively (panel b), indicating freezing and melting of water, respectively. The lower freezing T than T_m of water is merely supercooling.

The two difference spectra (panel c) on diagonally opposite sides have a mirror-image relation. In the T ranges of C1 and H3, water is in the liquid state. The negative/positive ($\sim 3600/$

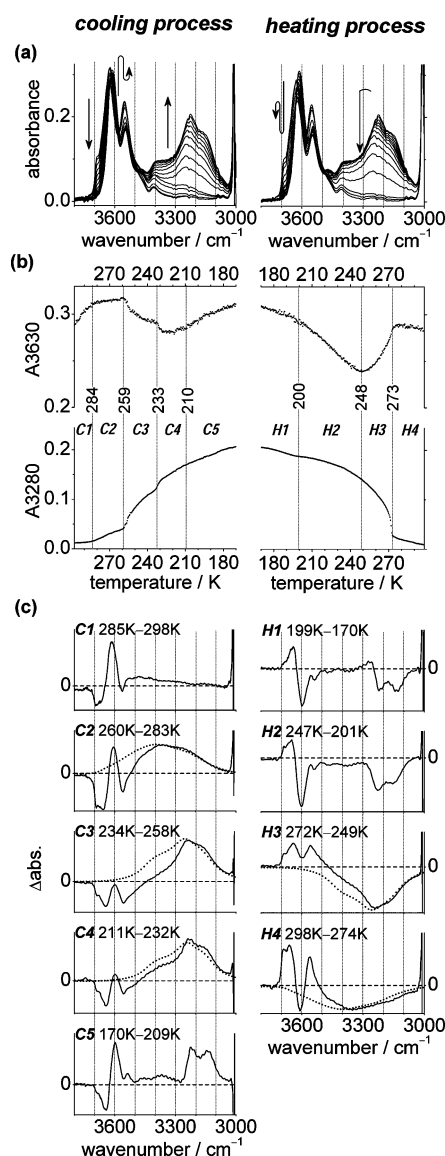


Figure 3. T dependence of MIR spectra of water sorbed into poly(*n*-butyl methacrylate): (a) original spectra at every ~ 10 K from 298 to 170 K; (b) T dependence of A_{3280} and that of A_{MONO} ; (c) difference spectra in each T range.

~ 3450 cm^{-1}) bands observed during cooling indicate that water molecules make a more associated form by T reduction.^{35–37} At the liquid–solid transition (C2 and H2), a clear peak at ~ 3250 cm^{-1} and two shoulders at ~ 3400 and ~ 3150 cm^{-1} and an asymmetric band at ~ 3500 cm^{-1} with opposite signs were observed. As clearly seen in the original spectra (panel a), both the clear peak and the two shoulders should be characteristic bands for ice. In the T ranges of C3 and H1, water is in the solid state (ice). A symmetric band at ~ 3450 cm^{-1} and two sharp bands with opposite signs at 3230 and 3150 cm^{-1} indicate the exchange from/to weakly H-bonded water molecules to/from strongly H-bonded ones by cooling/heating.

B. Sorbed Water (Figures 3 and 4). Cooling Process. An increase in MIR absorption of sorbed water and a red-shift of the characteristic band of the bridging water at ~ 3615 cm^{-1} were observed (panel a). If the red-shift is accompanied by the increase, the positive peak in the difference spectra (panel b)

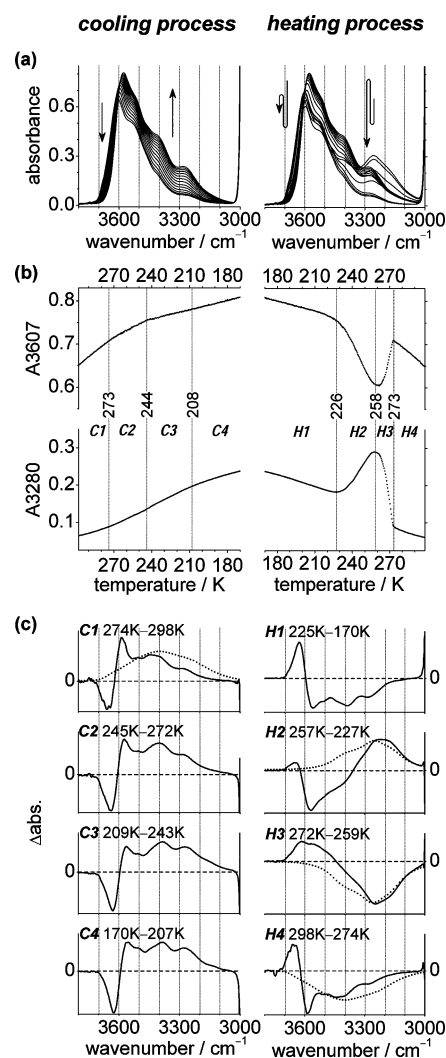


Figure 4. T dependence of the MIR spectrum of water sorbed into poly(2-ethoxyethyl methacrylate). The figure caption is the same as that for Figure 3.

should be larger than the negative one. The difference spectrum of pBMA in the T range of C1 (Figure 3) is a typical case of this. However, in many cases, negative/positive peaks with comparable intensities or no positive peak were observed. These results clearly indicate that the sorbed water changes from the monomeric state to the associated one. In the cases of pEEMA (Figure 4) and pMA (Figure S1, Supporting Information), the negative/positive peaks at $\sim 3650/\sim 3600$ cm^{-1} of the difference spectra in all T ranges (panel c) have comparable intensities. Their spectral profiles in the low frequency region resemble neither the original spectrum of pure water (dotted line) nor that of ice. In addition, no drastic change in A_{3280} was observed (panel b). These changes suggest that most of the sorbed water has no change in the state such as condensation or crystallization and that a part of the sorbed water becomes a small water cluster by cooling.

In marked contrast to the above cases, drastic changes in A_{3280} and A_{MONO} in the cases of pBMA (Figure 3) and pEEA (Figure S2, Supporting Information) were observed. In the T range of C2, a broad absorption of the difference spectra (panel b) in the low frequency is similar to the original spectrum of pure water (dotted line). The values of A_{3280} and A_{MONO} increase gradually and level off, respectively. The level-off in

Table 2. Change in the State of the Sorbed Water Observed Spectroscopically

polymer	pMA ^a	pBMA ^a	pEEA ^a	pEEMA ^a	pMMA ^b	pBA ^c	pMEA ^d	PS ^e
cooling process								
condensation		yes	yes			yes		yes
freezing		yes	yes			yes		yes
vapor deposition		yes	yes			yes	yes	yes
heating process								
vapor redeposition (recrystallization)	yes	yes	yes	yes			yes	yes
sublimation	yes	yes	yes	yes		yes	yes	yes
melting		yes				yes		yes
vaporization		yes				yes		yes
T_{ic} (K)	240	200	215	226			218	180

^aThis work. ^bReference 30. ^cReference 47. ^dReference 48. ^eReference 29.

A_{MONO} means a decrease of the bridging water. These results exactly exhibit the change of sorbed water from the monomeric state to the liquid state. In the T range of C3, the similarity of difference spectra to the original spectra of ice (dotted line) in the low frequency region is evidence of the formation of ice. A steep but not discontinuous change in A3280 is different from the case of pure water. There are two possible explanations for this: one is that there is a freezing distribution depending on random fluctuation in the arrangement of nearby water molecules in the liquid state, and another is that the bridging water is changed directly to ice without condensation. The latter process is denoted as “vapor deposition”. The distribution of freezing point has been reported to be no more than ~ 5 K,^{38–41} strongly suggesting that this slow crystallization is caused mainly by vapor deposition. Two pieces of spectral evidence for this process are the decrease in A_{MONO} synchronizing with the increase in A3280 and the absence of a positive peak in the high frequency region in the difference spectra. In the T range of C4 for pBMA, vapor deposition should be the sole process for the growth of ice because the difference spectrum is superposable on the original spectrum of ice (dotted line). In the lowest T range for pBMA (C5) and pEEA (C4), the difference spectra in the low frequency region are almost the same as the spectrum of ice, which exhibits no more change in the state of the sorbed water in this T range (although there is change in the state of ice already formed).

Heating Process. If recrystallization of the sorbed water occurs, the increase in the value of A3280 (or the decrease in the decreasing ratio of A3280) might be observed. Furthermore, if recrystallization is not devitrification but vapor re-deposition, the enhancement of the decrease in the value of A_{MONO} should be observed at the same time.

In the lowest T range (H1), the spectral changes were a mirror image to those in the lowest T range of the cooling process, indicating that the state change in the T region is in the opposite direction of that in the cooling process. In the next T range (H2) for pEEMA (Figure 4), pMA (Figure S1, Supporting Information), and pEEA (Figure S2, Supporting Information), the decrease in A_{MONO} was enhanced and the value of A3280 increased. In the two cases for pEEMA and pMA, although no ice formation during cooling was observed, a large negative band in the difference spectra in the T range of H3 is similar to the spectrum of ice in the opposite sign (dotted line). This clearly confirms the decrease in ice in the T range of H3 and the presence of ice at the low side of this T range. The increase in A3280 in the T range of H2 for the three polymers, therefore, corresponds to the growth of ice. This is just recrystallization of the sorbed water. It is noted here that the

increase in A3280 coincides with the enhancement of the decrease in A_{MONO} . This suggests that recrystallization is a direct change from the bridging water to ice. This process is denoted as “vapor re-deposition”.⁴²

In the case of pBMA (Figure 3), the change in A3280 and the difference spectrum in the T range of H2 are different from the above three cases, although enhanced decrease in A_{MONO} is observed. An increase in A3280 was not observed, but the rate of decrease in A3280 became smaller. The value of A3280 for ice decreases linearly until melting (right of panel b in Figure 2). This suggests that the decrease in the rate of decrease in A3280 means growth of ice. Therefore, the change in A3280 observed in the case of pBMA also indicates growth of ice during heating. This growth of ice is also considered to be vapor redeposition because the enhanced decrease in A_{MONO} was obtained simultaneously.

As stated above, in the T range of H3, a large negative band being similar to the spectrum of ice in the difference spectra was observed in all cases. This clearly indicates a decrease in ice in this T range. It is noted here that the change in A3280 is different from that when ice melts (Figure 2): the change was very steep but not discontinuous. The very large positive peak attributed to the bridging water and the increase in A_{MONO} synchronizing with the decrease in A3280 indicate that most of the ice formed in the polymer matrix directly transforms to the bridging water. This process is denoted as “sublimation”. However, in the cases of pBMA (Figure 3) and pMA (Figure S1, Supporting Information), the difference spectrum had a very broad negative band that is superposable on the original spectrum of liquid water (dotted line) in the next T range (H4). This suggests that a part of the decrease in ice in the T range of H3 in pMA and pBMA is melting and this liquid water is vaporized in the T range of H4. On the other hand, a liquid-like spectrum of water was not observed in the difference spectra of pEEMA (Figure 4) and pEEA (Figure S2, Supporting Information) in any of the T ranges, indicating that the decrease in ice in the two polymers should be only by sublimation.

DISCUSSION

Change in the State of Sorbed Water. All of water sorbed into the non-water-soluble polymers by vapor sorption has been widely considered to be the nonfreezing water. In other words, water molecules are maintained in the monomeric state at any T . This is mainly based on DSC analysis. No DSC signal from water sorbed into pBMA,¹⁵ poly(*n*-butyl acrylate) (pBA),²⁰ and pMEA²⁰ as the analogue of pEEA and pEEMA has been reported. However, in the first place, there are not

many reports on sorbed water by vapor sorption on the basis of DSC analysis. This might be because many researchers (including our research group) have been under the impression that the sorbed water should not be frozen. Besides, MIR spectroscopic analysis of various hydrated poly(meth)acrylates^{19–22,43–46} at room T has also abundantly reported the same interpretation. These spectral profiles of the sorbed water including the four polymers in this study (Figure 1) did not resemble that of pure water at all. The large difference hardly allows us to consider the change in the state by T . In our previous reports on several kinds of poly(meth)acrylates^{19,45} at room T , we also imprudently had the same interpretation without examining the T dependence of MIR spectra of the sorbed water.

As mentioned above, it should be correct that the sorbed water is in a monomeric state at room T . However, the present results and our recent studies on poly(methyl methacrylate) (pMMA),³⁰ pMEA,²⁹ pBA,⁴⁷ and polystyrene (PS)⁴⁸ by T variable MIR spectroscopy demonstrate that the change in the state by T is an undeniable fact. That is to say, the fact that the sorbed water is in a monomeric state at room T should not always mean that all of it is nonfreezing water. Changes in the state observed spectroscopically, including changes observed in our recent studies, are summarized in Table 2. These changes should be observed as a DSC signal if DSC sensitivity is high enough to detect all of the heat flux in the system (although it might be difficult for the current apparatus generally used).

Heat flux with condensation/vaporization of the sorbed water, nevertheless, might be more difficult to detect by DSC without the relation to its sensitivity. This is because the vaporization/condensation enthalpy of pure water, ± 44.9 kJ·mol⁻¹ at 273 K,²³ is comparable to the sorption/desorption ones of water molecules to/from the non-water-soluble poly(meth)acrylates, ~ 40 kJ·mol⁻¹ at room T , in opposite signs.⁴⁷ Condensation/vaporization of the sorbed water should be accompanied by desorption/adsorption of water molecules from/to the polymer chain, resulting in the two enthalpies canceling out each other. For the same reason, with sublimation/vapor deposition (including vapor re-deposition), the DSC signal expected from the sublimation/vapor deposition enthalpy of pure water, ± 50.8 kJ·mol⁻¹ at 273 K,²³ should not be obtained but only that near the melting/freezing enthalpy of pure water, ± 6.0 kJ·mol⁻¹. These phenomena have been demonstrated in the hydrated pBA system by highly sensitive DSC and T variable MIR spectroscopy.⁴⁷ These situations frequently lead to a completely misleading interpretation that liquid water (condensed water) is present at room T .

Various changes in the state given in Table 2 might hardly be accepted from the viewpoint of interpretation on the basis of DSC analysis. However, if accepting that the polymer chains are a part of the components of a small holed cage confining water molecules and that the polymer matrix is only an assembly of the cages, the phenomena observed here might not be strange. This is because the three states of matter (solid, liquid, and gas) depend only on the chemical potential: the matter has an association tendency with T reduction.⁴⁹ It is also clear, on the other hand, that the polymer chain sterically and physically (due to electrostatic interaction (H-bonding interaction)) affects the diffusion of water molecules and the association between water molecules. The degree of the effect should be dependent on the glass transition T (T_g) and the number of electrostatic interaction sites (oxygen atoms).⁵⁰ The number of

oxygen atoms per unit volume of polymers calculated from the density of polymers^{51–56} and its chemical formula is given in Table 2. In general, the greater the number of H-bonding sites is, the more inhibited are the diffusion and the association. The greater the reduction in T_g 's is, on the other hand, the less inhibited is the diffusion.

Although exact estimation of change in the state is difficult, some tendencies can be obtained: (1) a polymer with high T_g and many H-bonding sites such as pMMA shows no change in the state; (2) a polymer with low T_g and few H-bonding sites such as pBA shows change in the state except for recrystallization (vapor re-deposition); (3) a polymer with high T_g and few H-bonding sites such as pBMA and PS shows all of the changes in the state including recrystallization (vapor re-deposition); and (4) a polymer with low T_g and many H-bonding sites such as pMEA, pMA, and pEEMA shows no liquid state but crystallization. More discussion on recrystallization (vapor re-deposition) is presented below.

Recrystallization (Vapor Re-deposition). Recrystallization of water has been believed to be rare for non-water-soluble polymer systems. There are some reports about recrystallization of water for a highly concentrated aqueous solution of polymers,^{24–28} but as far we know, there have been only two reports for non-water-soluble polymer systems (pMEA¹⁰ and pTHFA¹⁴). Regardless of their water solubilities, recrystallization was considered to be devitrification, which is the change from glassy water to ice during heating. Devitrification, of course, is observed in the case of pure water, but a special technique such as a hyperquenching method is required.^{57–59} Recrystallization of water (maybe devitrification) observed in aqueous polymer solutions also generally requires rapid cooling.^{24–28} On the other hand, in the cases of pMEA and pTHFA, recrystallization was demonstrated by DSC even at a slow cooling rate of 2.5 K·min⁻¹.^{10,14} Furthermore, our recent study on pMEA²⁹ and the present results for the four polymers demonstrated recrystallization at extremely slow cooling rates of 0.25 and 0.5 K·min⁻¹, respectively. These phenomena are very interesting and worth special attention if it is true that recrystallization in their polymer matrixes is devitrification. As demonstrated by the results, however, the T dependence of MIR spectra clearly indicates that recrystallization is vapor redeposition and not devitrification. This is also supported by the dissimilar spectra in all T ranges to those of glassy water⁶⁰ and low-density liquid water.⁶¹ Devitrification and vapor redeposition are the same in the point that crystalline water is formed during heating, but the two phenomena are essentially different.

The recrystallization by vapor re-deposition might be related to the balance between flexibility of the polymer chain and strength of the electrostatic interaction with water molecules. Figure 5 shows a plot of starting T 's of recrystallization of water, T_{rc} 's (Table 2), against T_g 's of the polymers. In the cases of the polymers with high O atom density and low T_g (pMA, pEEA, pEEMA, and pMEA), the value of T_{rc} increased with an increase in T_g . This tendency could be explained as follows: the diffusion of the bridging water, which is restricted to the electrostatic interaction sites below T_g of polymers, is spuriously enhanced with the increase in flexibility of the polymer chains during heating (that is, glass-to-rubber transition of the polymer), resulting in enhancement of the association between water molecules, and then if T at that moment is lower than T_m of water, the bridging water might be recrystallized (vapor re-deposited). The reason why T_{rc} 's are

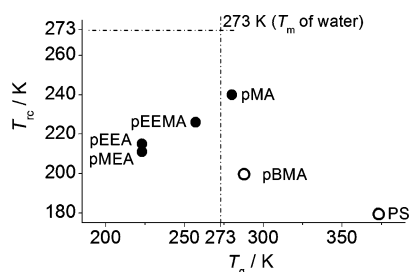


Figure 5. Relation between starting T of recrystallization of water in various polymers and their T_g .

lower than T_g 's is that T_g 's are not defined as starting T 's of glass-to-rubber transition, which should be lower than T_g 's.⁶²

In the cases of polymers with relatively high T_g and low O atom density (pBMA) and without O atom (PS), T_{rc} 's decreased with an increase in T_g . In contrast to the above cases (pMA, pEEA, pEEMA, and pMEA), this tendency might be related to only strength of the electrostatic interaction rather than flexibility of the polymer chain. This is because their T_g 's are higher than T_m of water by more than 20 K and therefore the polymer chain is considered to be completely in the glass state at their T_{rc} 's. It might be better to consider that recrystallization (vapor re-deposition) in the two cases occurred when the diffusion force of water molecules exceeded the restriction force by the electrostatic interaction. That the diffusion force of any molecules increases with heating is the physicochemical requirement. The electrostatic interaction of O atoms in (meth)acrylate polymers with water molecules should be much stronger than that of π -electrons of the phenyl ring in PS.⁶³ This order does not conflict with the order of T_{rc} for them.

The consideration mentioned above means that the recrystallized water is merely the bridging water, which should be condensed and/or vapor-deposited through the diffusion during cooling and which might be retained at T at which the water molecules could not diffuse due to a high cooling rate. It also means that the mass of the recrystallized water is decreased at slower cooling and is not observed at infinitely slow cooling because the sorbed water should be frozen during cooling. Strong dependence of the mass of the recrystallized water in pMEA and PS on cooling rate has been reported: the slower cooling rate diminished the mass of the recrystallized water.

CONCLUSION

After the two reports for recrystallization of water in non-water-soluble polymers (pMEA and pTHFA) on the basis of DSC analysis, recrystallization was newly demonstrated spectroscopically in four poly(meth)acrylates in this study. The four cases clearly indicate that recrystallization is no longer a rare phenomenon. In addition, different from aqueous polymer solutions, all of the recrystallization observed in this study is not devitrification but vapor re-deposition. Needless to say, condensed water with a special structure to recrystallize in non-water-soluble polymers does not exist at physiological T . Furthermore, recrystallization of water is not related to the biocompatibility of polymers. It rather depends on the balance between flexibility and strength of the electrostatic interaction of polymers with water molecules.

ASSOCIATED CONTENT

Supporting Information

Temperature dependence of the MIR spectra for pMA and pEEA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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