

# An Analysis of Capillary Water Behavior in Poly-*p*-Phenylenebenzobisoxazole Fiber

TOORU KITAGAWA, KAZUYUKI YABUKI

Polymer Research Department, Toyobo Research Center Co., Ltd., 2-1-1, Katata, Ohtsu City, Shiga, 520-0292 Japan

Received 20 January 2000; accepted 7 June 2000

**ABSTRACT:** This study concerns with analysis of water inside a poly-*p*-phenylenebenzobisoxazole (PBO) fiber. It is important to analyze the state of water attached to polymer, because it may affect properties of fibers as the increase of drying speed of water from the fiber. To carry out such observation, differential scanning calorimetry and nuclear magnetic resonance spectroscopy were applied. They reveal the large freezing point depression and the state of water inside wet PBO fiber. It shows extraordinary low crystallization temperature. The reason may be that the water is packed into capillary voids whose diameter is around 2–3 nm. Proton NMR analysis also suggests the above result. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1030–1036, 2001

**Key words:** poly-*p*-phenylenebenzobisoxazole fiber; capillary water; differential scanning calorimetry; nuclear magnetic resonance; small angle X-ray scattering

## INTRODUCTION

Interaction between water and polymer has been an important concern in the polymer industry, because it affects properties of plastic product. One such example concerns analysis of drying solvent from fiber. Many fibers such as acrylic and regenerated cellulose fibers are spun with a wet spinning method, in which fiber structure formation happens and is determined in the coagulation and following drying processes. In the cases of acrylic fibers, aqueous solution is used as a coagulant and washing fluid, and the interaction force between the water and the polymer determine fiber structure, especially capillary diameter and shape, which result in fiber properties.<sup>1–3</sup> Poly-*p*-phenylene terephthalamide (PPTA) is also one such fiber made through a coagulation pro-

cess from strong acid polymer solution, and recently poly-*p*-phenylenebenzobisoxazole (PBO) fiber has been developed and commercialized as a high-modulus and high-strength fiber.<sup>4</sup> They are made through a dry-jet wet spinning method with a rigid-rod polymer, and the produced fiber structure also shows the presence of capillaries elongated to the fiber axis. The presence of capillary and its diameter were inspected with small-angle X-ray scattering (SAXS) and transmission electron microscopic (TEM) techniques.<sup>5,6</sup> The values were reported as around 3 nm (PPTA)<sup>5</sup> and 2–3 nm (PBO)<sup>6</sup> which are far less than those of acrylic<sup>1,2,7</sup> and cellulose<sup>8</sup> fibers reported. Water absorbed in as-spun fiber may be localized in the capillary before drying in the production process. But those SAXS and TEM techniques do not provide information on which kind of force is acting on water inside the fiber.

In order to make the thermodynamic state of water clear, <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy<sup>9</sup> and differential scanning

Correspondence to: Tooru Kitagawa (tooru\_kitagawa@kt.toyobo.co.jp).

*Journal of Applied Polymer Science*, Vol. 80, 1030–1036 (2001)  
© 2001 John Wiley & Sons, Inc.

calorimetry (DSC) have been effective methods.<sup>10</sup> Bulk water freezes at 0°C under normal pressure but it shows an extraordinarily large freezing point depression if it is packed in very small capillary, especially its diameter goes down below 10 nm. The effect is considered to be a reflection of the surface tension of that small droplet. Todoki and Ishikiriya inspected such water in polymethyl methacrylate gel with DSC, and found a relationship between capillary diameter and the freezing point depression.<sup>10</sup> The freezing–melting behavior of capillary water can also be inspected with <sup>1</sup>H NMR spectroscopy by changing sample temperature. This measurement is due to the feature that NMR peak can be observable if the measured molecule is allowed for free movement. The degree of freedom (ease of movement) is expressed as NMR peak sharpness or relaxation times. There is a report<sup>9</sup> that the water in methacrylate hydrogel has freedom close to free water than chemically bound water. Konomi et al. characterizes the state of water absorbed in PPTA fiber.<sup>11</sup> Its molecule contains an OH— group (that is different from PMMA) and can interact with water molecule. The NMR result gives a broad peak indicating that the movement of water is limited by the interaction. Infrared radiation (IR) spectroscopy also becomes a useful tool to analyze the bound state between the water molecule and polymer with the aid of the normal mode vibration calculation. Kusanagi et al. analyzed the interaction between water and a polymer fiber such as polyethyleneterephthalate.<sup>12</sup>

In this study, the acting force on water in a capillary of PBO fiber is analyzed with DSC and NMR methods. PBO has no particular functional group in the molecule to interact with water as cellulose and PPTA, but there is always a problem of drying that water up in the fiber manufacturing process without destroying fiber structure.<sup>13</sup> To understand this difficulty and propose a solution to dry fiber easily it is inevitable to sum up not only morphological information but also acting forces on the water. But there was limited knowledge about behavior of the PBO capillary water. Therefore, this study is concerned with these matters.

## SAMPLE AND EXPERIMENT

Sample fiber containing water inside is taken up from the point after the washing process is finished in the PBO fiber production process. Then

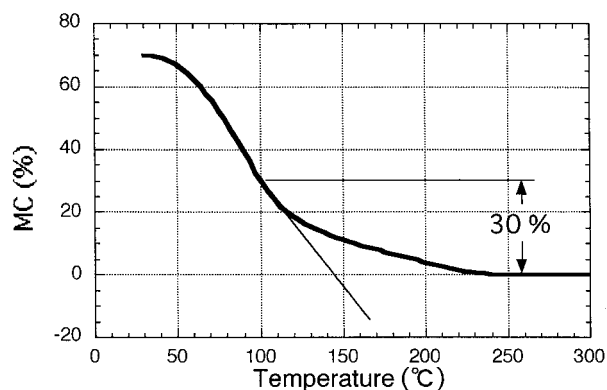


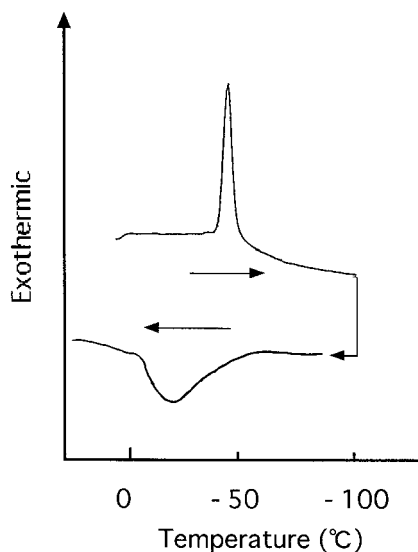
Figure 1 TGA curve for wet PBO fiber.

the fiber was stored in water before measurement to keep structure wet. For DSC and thermal gravitation analysis (TGA) measurements, a Mac Science MC-3100 analyzer was adopted. To measure DSC curves a weight of 3–10 mg of chopped fibers was sealed in an aluminum pan. An open platinum pan was used to weigh fiber in an oven in TGA. Some fibers were predried at 200°C in an air circulation oven to reduce water in the fiber before measurement in order to check moisture content dependence. A Varian XL-300 spectrometer (the power of 300 MHz) is used to detect the NMR spectrum. (Solid-state NMR mode is not applied in this study.) Specimen fibers were inserted in a NMR glass tube and the fiber axis was placed parallel to the magnetic field of the spectrometer. The NMR peak became wider in the case in which the measured fiber axis has a right angle with the magnetic field because of disturbance of the magnetic field due to oriented PBO polymer chains. Relaxation times (spin–lattice relaxation;  $T_1$  and spin–spin relaxation;  $T_2$ ) were also measured.

## RESULT AND DISCUSSION

### TGA Diagrams

Figure 1 shows weight loss of PBO wet fiber as a function of temperature. Fiber contains both capillary water inside and surface water outside around fiber filaments just after washing process. The wet fiber is heated at the rate of 20°C/min in a TGA oven. The weight goes down rapidly up to 120°C, which comes from evaporation of surface water. Over 120°C, it still shows some slope (weight reduction), though it becomes less, and levels off after 230°C, indicating that water inside the fiber is so constrained by some force that there



**Figure 2** DSC curve for predried PBO fiber at the moisture content of 20.8%.

is some water that remains there up to 230°C. An amount of the constrained water can be estimated from the weight loss between 100 and 230°C, and it is estimated about 30% in water (moisture) content (MC) that is calculated from the following:

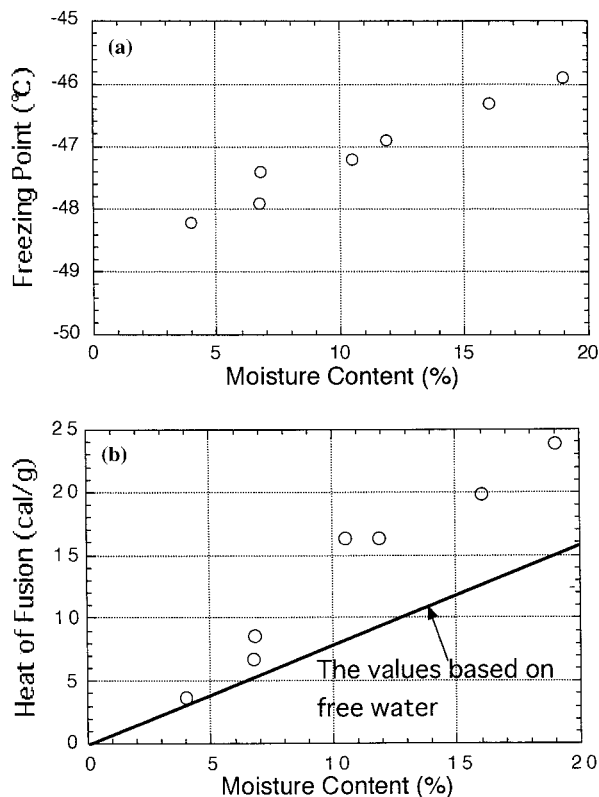
$$\text{MC} = \frac{\text{Fiber Weight containing water}}{\text{Fiber weight after dry} - 1} \times 100[\%] \quad (1)$$

### DSC Measurement

The freezing point of capillary water can be measured by DSC and the result is shown in Figure 2. From the room temperature, chopped PBO fiber (containing 24% water) is cooled at the rate of 10°C/min up to -100°C and then heated back to room temperature. In the figure we can understand that the water freezes suddenly at -45°C in the cooling process and melts again over the region from -40 to -10°C gradually in the thawing process. Brun et al.<sup>14</sup> and Todoki et al.<sup>10</sup> reported the freezing point depression relating to the diameter of water that is packed into a small space. As the diameter of water droplet becomes smaller (less than 10 nm, especially), the effect from surface tension is not so negligible thermodynamically that the large freezing point depression can be observable. It is noteworthy that the PBO molecule does not contain a special group that can bond water molecules such as poly-*p*-phenylene terephthalamide (PPTA). These theories give us

the equations relating the freezing point depression to the radius of the diameter of capillary. According to the theories, the water inside the PBO fiber is packed into a small space whose size is less than 3 nm. We have already reported that PBO AS fiber contains a capillary void elongated to the fiber axis, whose diameter is 2–3 nm by SAXS.<sup>6</sup> Combining the two facts we also see that water in the PBO fiber should lie in capillary. Large supercooling phenomena was also confirmed between cooling and thawing processes, and peak shape (crystallization) in the cooling process is sharper than that (fusion) of the thawing process. The reason is not understood well but the fact that capillary water is compartmentalized into a small room may be one of the reasons. The above result indicates that water in the PBO fiber should be bound not chemically but physically (surface tension). This point is proved again by NMR below.

In order to put further comprehension on the bound state of capillary water to PBO fiber, the freezing point depression dependence on the water (moisture) content was measured [Fig. 3(a)]. The dependence is rather weak. It may be because the water is made into more localized-compact droplets as water content is lowered. Heat of fusion, which has linear correlation with freezing peak integral intensity in DSC curve, is plotted against moisture content [Fig. 3(b)]. The solid line in the figure represents the state at which the internal water behaves as bulk free water (the heat of fusion ~ 80 cal/g; Ref. 15) In general, the state of water can be grouped into three types: bulk (free), intermediate (freezable bound), and bound (nonfreezing) waters. Nakamura et al. estimated the amount of nonfreezing water in polyhydroxystyrene derivatives from this plot.<sup>16</sup> The molecule contains hydrogen bonding, and such water chemically connected to this group cannot behave freely as free water and intermediate water. The bound water cannot crystallize if the sample is cooled below the freezing plot. In fact, the plot reveals that the derivatives contain 2–8% of nonfreezing water. Contrary to this general nonfreezing water behavior, the data plots in Figure 3(b) converges into 0 at zero moisture content while the measured data points deviate from the solid line over 7% of moisture content. This indicates that PBO fiber contains almost zero amount of nonfreezing water at the region near zero moisture content, but there may coexist some bound water with intermediate water at high moisture content regions. These observations also suggest

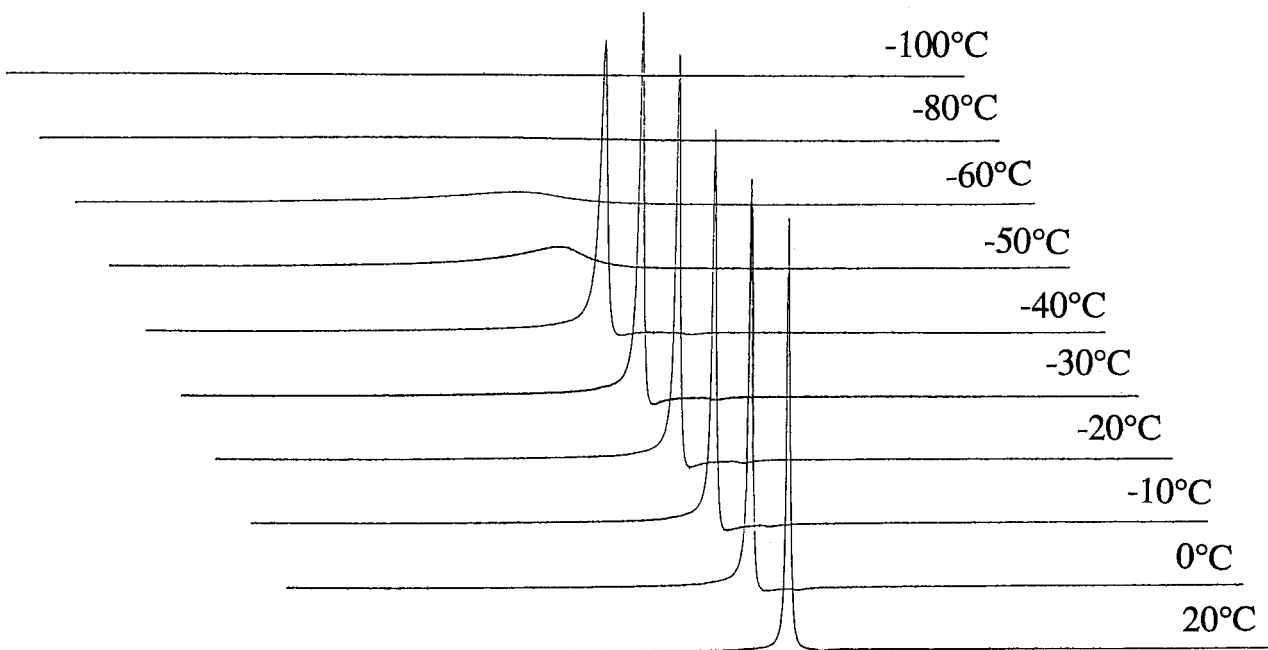


**Figure 3** (a) The freezing point depression of the capillary water dependence on the water (moisture) content. The temperature is determined from the peak top of crystallization peak in DSC curves. (b) Water (moisture) content dependence on the heat of fusion of the crystallization peak.

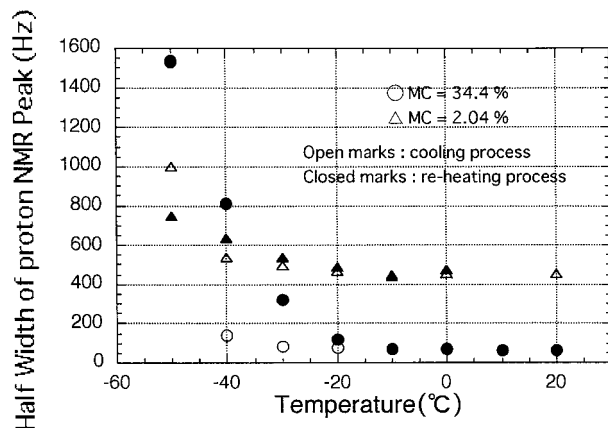
that water in PBO fiber is located in the capillary (the diameter is 2.4 nm by SAXS), and the source to the fiber is surface tension and not chemical bond. It is noted that the question about the drying to reduce moisture content without destroying the fiber structure remains unclear. The disagreement of the heat of fusion of the internal water against free water may be involved.

### NMR Analysis

Figure 4 shows proton NMR peaks from PBO fiber containing water inside before drying (at the moisture content of 34.4%). The measurement temperature was varied from 20 to  $-100^{\circ}\text{C}$ . We can confirm sharp peaks from 20 to  $-40^{\circ}\text{C}$ , but below this temperature the peaks become diffuse (at  $-50$  to  $-60^{\circ}\text{C}$ ) and disappear (below  $-80^{\circ}\text{C}$ ). This indicates that the water starts to crystallize around  $-40^{\circ}\text{C}$ , which is confirmed as the same temperature as the DSC result in the previous section. But the DSC curve in the cooling process is not optimal, especially in stability of the baseline, so that both the crystallization temperature values estimated by DSC and NMR will not meet exactly. As mentioned above, these peak widths correspond to the degree of freedom on capillary water motion. To analyze this change quantitatively, the half width of the peaks is calculated and the results are plotted in Figure 5. We can confirm clearly that the half width become wide

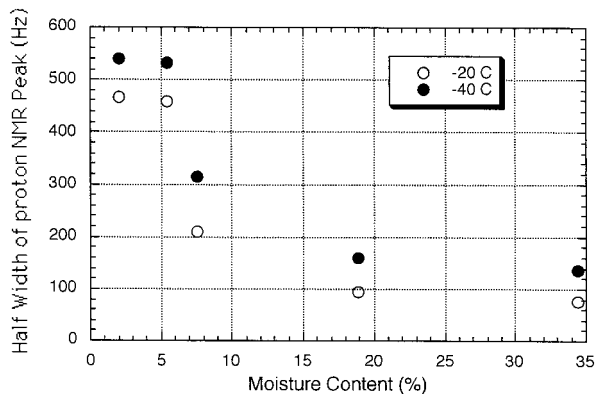


**Figure 4**  $^1\text{H}$ -NMR peak of water in PBO fiber.

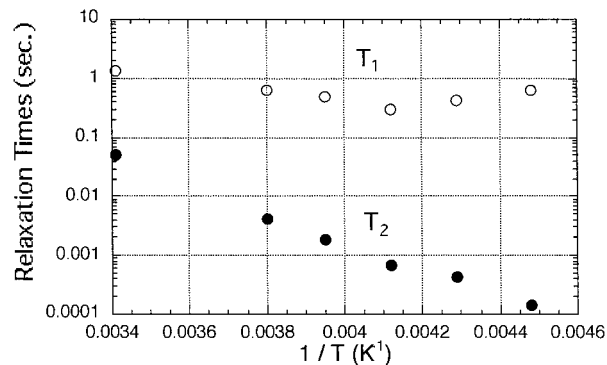


**Figure 5** Half width of  $^1\text{H}$ -NMR peak of water in PBO fiber.

as the fiber is cooled. This indicates that the freedom of capillary water is abruptly constrained after crystallization occurs. When the fiber is reheated, the peak width becomes sharp but the trajectory in Figure 5 does not trace to the cooling process from  $-20$  to  $-50^\circ\text{C}$ , which is the same hysteresis behavior as the DSC curves (supercooling effect). This extraordinary low crystallization temperature is the same irrespective of moisture content region (34–2%), though we do not show the all data sets. Moisture content dependence on half width is shown in Figure 6. It can be seen that peak width becomes wider as moisture content decreases. This means that the degree of freedom of capillary water becomes less. The reason is that space occupied by capillary water is a more limited narrow space as water content decreases. This tendency is the same over the temperature range from  $20$  to  $-40^\circ\text{C}$  more. We see



**Figure 6** Water (moisture) content dependence on half width of  $^1\text{H}$ -NMR.



**Figure 7**  $^1\text{H}$ -NMR relaxation times of water in PBO fiber

that peak width changes from  $60$  Hz ( $\text{MC} = 34\%$ ) to  $500$  Hz ( $\text{MC} = 2\%$ ) at that temperature range. This moisture content dependence has been confirmed in cellulose, whose half width of NMR peak is wider than PBO capillary water.<sup>17</sup> Kusanagi et al. studied behavior of water attached to fiber and reported that the half width of bulk free water shows the value of  $6$  Hz, while that of bound water is more than  $1000$  Hz.<sup>18</sup> In this case we can understand that PBO capillary water shows the state between free water and bound water while it still shows crystallization with extra low freezing point depression around  $-50$  more. In order to inspect this movement of capillary water further quantitatively, relaxation times ( $T_1$  and  $T_2$ ) of wet PBO fiber were adopted and measured. The  $180^\circ\text{-}\tau\text{-}90^\circ$  pulse technique is adopted for  $T_1$  measurement and the Carr–Purcell–Meiboom–Gill method is used for  $T_2$  measurement. Spin–spin relaxation time ( $T_2$ ) is more directly concerned with the freedom of molecular movement and width of NMR peak, as in the following equations,

$$1/T_2^* = 1/T_2 + 1/\Delta \quad (2)$$

$$\delta\nu_{1/2} = 1/\pi T_2 \quad (3)$$

where  $\delta\nu_{1/2}$  is the width of NMR peak,  $1/\Delta$  the broadening factor due to instrument adopted. The result is summarized in Figure 7. It is useful to estimate correlation time  $\tau_c$  from  $T_1$ , because the time defines the length of time that the molecule can be considered to be in a particular state of motion. The estimated correlation time is on the order of  $10^{-11}$  s, indicating that the water in PBO capillary behaves closely as free water ( $\tau_c \sim 10^{-11}\text{--}10^{-12}$  s).<sup>9,18,19</sup> (If it is bound chemically



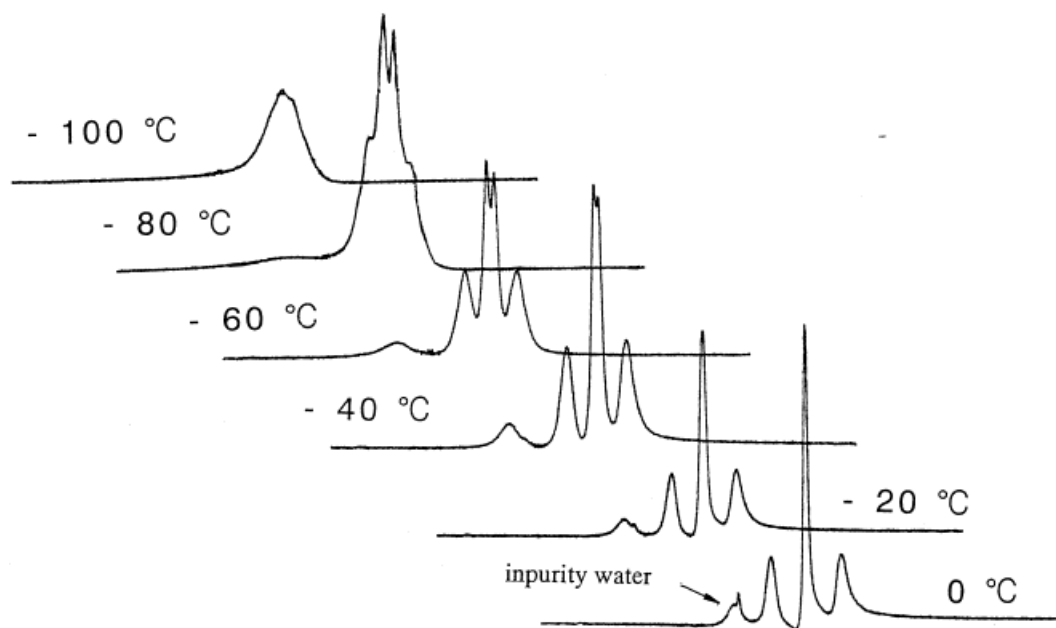


Figure 8  $^1\text{H-NMR}$  peaks of acetone in PBO fiber.

to the polymer chain, the correlation time lies in the range  $10^{-6}$ – $10^{-9}$  s.) It is noteworthy that the measured  $T_2$  decreases as the temperature goes down, showing that the freedom of the water molecule becomes limited and crystallized in end.

Finally, connectivity of capillary water between independent capillaries over the radial direction in the cross-section of the fiber is checked by the following dipping method, because, for example, ease of molecular migration from the center of the PBO fiber to the surface is an important factor for drying fiber moisture with limited time. For such purpose the wet fiber was dipped and kept in excessive acetone for a few seconds, and then proton NMR measurement for the dipped fiber was carried out. The resultant NMR spectrum is shown in Figure 8. The acetone peaks could be observed together with a water peak of impurity. It is noteworthy that most internal water can be replaced with acetone in a few seconds with just dipping. The acetone molecule has six protons inside the chemical structure formula, and they are equivalent in the liquid state because movement and exchange of proton is so rapid in that state. But the figure shows split proton peaks, suggesting that some factors that inhibit such exchange may be emphasized. (The small peak in the leftmost side from 0 to  $-60^\circ\text{C}$  most comes from impurity of water.) In fact, some reports propose that even proton NMR peaks of methanol (which shows one steep peak in bulk

liquid state) give a split pattern if the molecular movement is constrained in a certain force.<sup>19,20</sup> One explanation for this is as follows: If the molecule is cooled, the energetic potential peak for the exchange of molecular conformation becomes relatively high, which places two different protons in the molecule in the magnetic state as a result. Therefore, they become observable as the above-mentioned peak split.

As Martin et al. has already reported, fiber made of rigid-rod polymer is an assembly of elongated microfibrils.<sup>21</sup> The structure becomes solid as the production process goes from coagulation, drying, to heat treatment. There is a space between the microfibrils to accommodate water molecules inside fiber. In the case of acetone in PBO fiber, we may conclude that the surrounding acetone replaces internal water in dipping within a short period and then fills the capillary. Also, exchange of proton (rotating of the methyl group around the carboxyl axis and rotating the proton in the methyl group) in the molecule is limited due to a small space less than 3 nm. Acetone is so symmetric a chemical structure that there is no such inhomogeneity of magnetic field. The triplet or quartet split may be due to spin–spin coupling interaction of protons in the acetone molecule. This idea should be denied in the normal bulk state and further inspection is necessary to put a complete explanation on this interesting capillary acetone's behavior.

## CONCLUSION

In this study the thermodynamic state of water included in PBO fiber has been examined with DSC and NMR methods. They prove that the water shows an extraordinary large freezing point depression, indicating that it suffers from a certain force. As the water is divided into a small part (capillary) below 3 nm in diameter, the effect of surface tension becomes hard to be negligible and the freezing point depression can be observable. There is no special chemical bond between the water and PBO molecule. The water is categorized into freezable bound water, which has the freedom of bulk water but suffers large surface tension. Sharp proton NMR peaks and measured relaxation times values also suggest this conclusion.

We express gratitude to Mr. T. Mizukami for his support of DSC measurement and analysis. Mr. K. Teramoto, Mr. T. Ichiryu, and Mr. Y. Tanaka gave useful comments and had fruitful discussions with us. Thanks are also extended to Dr. A. Kaji for his introduction and guidance of NMR measurement and analysis.

## REFERENCES

1. Craig, J. P.; Knudsen, J. P.; Holland, V. F. *Text Res J* 1962, 32, 435.
2. Knudsen, J. P. *Text Res J* 1963, 33, 13.
3. Dumbleton, J. H.; Bell, J. P. *J Appl Polym Sci* 1970, 14, 2402.
4. Yabuki, K. *Look Japan* 1985, August, 24.
5. Dobb, M. G.; Park, C. R.; Robson, R. M. *J Mat Sci* 1992, 27, 3876.
6. Kitagawa, T.; Murase, H.; Yabuki, K. *J Polym Sci Polym Phys* 1998, 36, 39.
7. Bohn, C. R.; Schaeffgen, J. R.; Statton, W. O. *J Polym Sci* 1961, 55, 531.
8. Statton, W. O. *J Polym Sci* 1956, 22, 385.
9. Nosaka, A.; Ishikiriyama, K.; Todoki, M.; Tanzawa, H. *J Appl Polym Sci* 1990, 39, 2443.
10. Ishikiriyama, K.; Todoki, M.; Kobayashi, T.; Takeyama, T.; Tanzawa, H. *Polym Prepr Jpn* 1985, 34, 2645.
11. Konomi, T.; Yamamoto, Y. *Sen-i Gakkaishi* 1990, 46, 281.
12. Kusanagi, H.; Yukawa, S.; Ishimoto, A. *Polym Prepr Jpn* 1991, 40, 3482.
13. Ota, T.; Nanba, K.; Yamamoto, A. *Sen-i Gakkaishi* 1975, 31, 85.
14. Brun, M.; Lallemand, A.; Quinson, J.; Eyraud, C. *Thermochim Acta* 1977, 21, 59.
15. Barrow, G. M. *Physical Chemistry*, 4th ed.; McGraw-Hill International Book Company: Tokyo, 1979.
16. Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* 1983, 24, 871.
17. Ogiwara, Y.; Kubota, H.; Hayashi, S.; Mitomo, N. *J Appl Polym Sci* 1970, 14, 303.
18. Kusanagi, H. *Kobunshikakou* 1990, 40, 40.
19. Bovey, F. A.; Jelinski, L.; Mirau, P. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, CA, 1988.
20. Minagawa, M.; Shirai, H.; Morita, T.; Fujikura, Y.; Kameda, K. *Polymer* 1996, 37, 2353.
21. Martin, D. C.; Thomas, E. L. *Mat Res Soc Symp Proc* 1989, 134, 415.