Macromolecules **2008**, *41*, 3157−3161

Mesomorphic Phase of Poly(butylene-2,6-naphthalate)

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Received October 27, 2007; Revised Manuscript Received February 15, 2008

ABSTRACT: The mesomorphic phase of poly(butylene-2,6-naphthalate) (PBN) has been studied using wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). It was found that PBN showed a mesomorphic phase when it was rapidly quenched from the molten state to 0 °C. The mesomorphic PBN was nearly transparent solid in appearance and its structure in WAXD scale was an intermediate one between amorphous and crystal having smectic periodicity. With increasing the temperature, a portion of amorphous remaining in the quenched PBN transformed into the mesomorphic phase above 48 °C, and then the mesomorphic phase began to transform into the α-crystal above 71 °C. We propose that the mesomorphic phase of PBN has a glass transition temperature T_g^{meso} at 65 °C besides the normal glass transition temperature T_g for the isotropic glass at 41 °C.

1. Introduction

Poly(butylene-2,6-naphthalate) (PBN) is one of crystalline polyesters. The monomeric unit of PBN consists of the flexible part, butylene, and the rigid part, naphthalate. Two kinds of crystal polymorphisms of PBN have been acknowledged as α- and β-forms up to the present.[1] The unit cell parameters of the α-form crystal are $a = 4.87$ Å, $b = 6.22$ Å, $c = 14.36$ Å (fiber axis), $\alpha = 100.78°$, $\beta = 126.90°$, and $\gamma = 97.93°$.[1] Those of the β-form are $a = 4.55$ Å, $b = 6.43$ Å, $c = 15.31$ Å (fiber axis), $\alpha = 110.1°$, $\beta = 121.1°$, and $\gamma = 100.6°$.[2]

The PBN is very easy to crystallize by just standing to cool from molten state; accordingly it is very difficult to obtain an isotropic glass, i.e., a frozen state of melt, by cooling. This characteristic is quite a contrast to the case of poly(ethylene terephthalate) (PET) within the crystalline polyesters. The crystal forms of PBN obtained by melt-crystallization below and above 215 °C are pure α-form and a mixture of α- and β-form, respectively. The respective morphologies in micrometer scale are a typical spherulite and a dendritic sphelulite.[3] Pure β-form is obtained near the melting point T_m (=ca. 240 °C).[3,4] A portion of the α-form transforms into the β-form by a uniaxial drawing or a thermal treatment.[1] Moreover, multiple melting behavior of the PBN crystals has been studied in detail[5,6] and the equilibrium melting temperature is reported to be 276 °C.[5] Thus, the crystallization behavior of PBN at small quenching depths has been extensively studied in the past.

However, the structure and thermal property of PBN at large quenching depths are not yet settled, because the fast crystallization rate of PBN at the large quenching depth makes it difficult to follow up the behavior at low temperatures. Probably due to the difficulty to obtain an isotropic glass, diverse values for the glass transition temperature (T_g) have been reported, such as 41,[7] 48,[8] 52,[9] 66,[10] 71,[11] and 82 °C.[12]

Isotactic polypropylene (iPP) is a crystalline polymer also having a fast crystallization rate. However, it can be solidified into an intermediate state between crystal and amorphous when a thin specimen of molten state is rapidly quenched.[13] Such an intermediate state of iPP is called "mesomorphic phase". Although the iPP has a flexible backbone, the mesomorphic phase of iPP shows a smectic-like structure.[13−16] The formation mechanism of the mesomorphic phase of iPP can be explained using that of the lyotropic liquid crystal by assuming helical segments of iPP chains play a role of mesogens.[15,17]

The motivation of this study is to investigate whether the PBN forms or not a mesomorphic phase similar to the mesomorphic phase of iPP by a rapid quenching method. The structure and thermal property of the rapidly quenched PBN are examined using a wide-angle X-ray diffraction (WAXD) and a differential scanning calorimetry (DSC).

2. Experimental Section

The materials for specimens were PBN pellets having an intrinsic viscosity of 1.40 dL/g.[18] The PBN sample sandwiched between thin Kapton films was melted at 280 °C ($>T_m$) for 5 min on a hot stage, and then rapidly quenched to 0 °C by dipping into ice–water. The thickness of the sample film was ca. 150 μm. With the aforementioned thickness and quenching, crystallization of PBN could be prevented as will be shown in the results. Thus obtained quenched PBN films in appearance were nearly transparent solid. For the one-dimensional wide-angle X-ray diffraction (1D-WAXD) measurements, the sample films 150 μm thick was piled 5-fold to ensure the scattering intensity. The quenched PBN sample stretched by four times was also prepared for two-dimensional wide-angle X-ray diffraction (2D-WAXD) measurements.

Both 1D- and 2D-WAXD measurements were performed using the beam line BL-40B2 at SPring-8, Nishiharima, Japan. The WAXD covers a range of scattering vector q ($=4\pi(\sin\theta)/\lambda$; λ and 2θ being X-ray wavelength and scattering angle, respectively) from 0.40 to 3.0 Å^{-1}. Temperature of the samples for the WAXD measurements was controlled using a Linkam CSS-450 high temperature shear cell without driving a shear unit. The sample films were heated up from room temperature to 260 °C at a rate of 4 °C/min in both 1D- and 2D-WAXD measurements.

The quenched samples, which were prepared in the same way as the WAXD's, were encapsulated in an aluminum-pan for DSC measurements. Normal DSC measurements were carried out with a PerkinElmer DSC7 at a heating rate of 4 °C/min. Storage part of temperature-modulated DSC (TMDSC) measurements were carried out with a Mettler Toledo DSC-822e at a heating rate of 1 °C/min.

3. Results and Discussion

3.1. Structure of Mesomorphic Phase of PBN. Parts a−c of Figure 1 show 1D-WAXD for the quenched PBN measured at room temperature, the molten PBN at 255 °C, and the crystallized PBN at 180 °C from the quenched state, respectively. A weak but sharp peak at $q = 0.44$ Å^{-1}, a strong broad peak at around $q = 1.4$ Å^{-1}, and shoulder peaks at $q = 1.0$ and 1.9 Å^{-1} are found in Figure 1a.

On the other hand, the sharp peak is not found, but only an amorphous halo is found at around $q = 1.35$ Å^{-1} in Figure 1b. Comparing parts a and b of Figure 1, the strong broad peak

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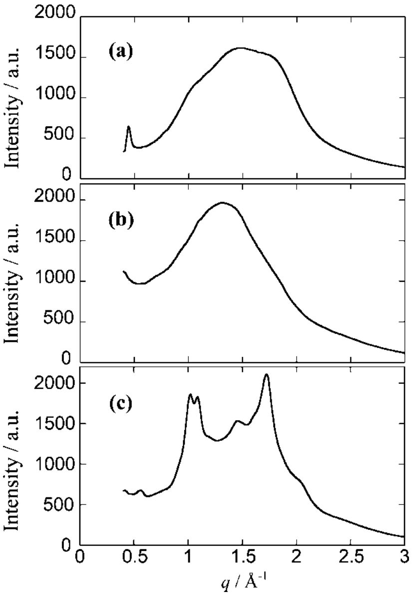

Figure 1. 1-Dimensional WAXD for a quenched PBN (nonstretched specimen) (a), a molten PBN at 255 °C (b), and a crystallized PBN at 180 °C from the quenched state (c).

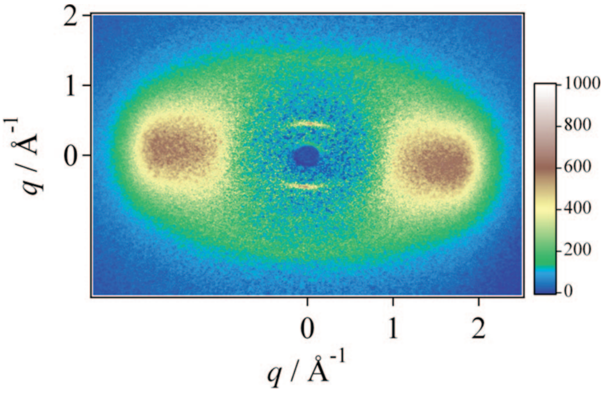

Figure 2. 2-Dimensional WAXD image for a four-times stretched specimen of the quenched PBN. The stretched direction is equal to the meridional direction in the image.

which was found in the quenched PBN (Figure 1a) is assigned to an amorphous halo. As will be discussed later, the position of the sharp peak at $q = 0.44$ Å^{-1} shifts to the higher q and decreases in intensity in the crystallized PBN (Figure 1c). Trace of the sharp peak in the quenched PBN was seen in an earlier work,[1] but it has not been studied in detail since then as far as the authors know.

In order to understand the origin of the sharp peak in the quenched PBN (Figure 1a), we have conducted 2D-WAXD measurements for a stretched specimen of the quenched PBN.

Figure 2 shows a 2D-WAXD image for the four-times stretched PBN measured at room temperature. Two sharp peaks in a lower angle and two broad peaks in a higher angle are observed along and perpendicular to the stretched direction, respectively. The amplitudes of the scattering vector of these peaks in the 2D-WAXD image are essentially the same as those in the 1D-WAXD for the nonstretched PBN (Figure 1a). Thus it has turned out that the sharp peak observed at $q = 0.44$ Å^{-1} in Figure 1a, corresponding to 14.3 Å in real space, is due to the diffraction by a longitudinal order in the quenched PBN. On the other hand, the broad peak at around $q = 1.4$ Å^{-1} in Figure 1a is due to the lateral interchains' correlation in the quenched PBN. The former peak is very sharp just like diffraction by a fiber period in a crystalline structure, but the latter one is as broad as the correlation in a liquid-like structure. These results suggest that the quenched PBN has some intermediate structure having smectic periodicity.

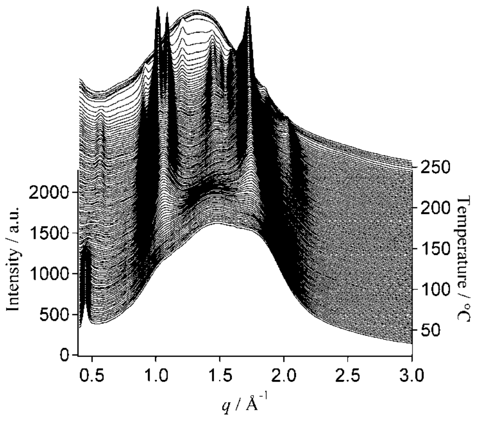

Figure 3. WAXD for the mesomorphic phase of PBN (nonstretched) during a heating process at a heating rate of 4 °C/min.

The diffraction pattern in Figure 2 shows a characteristic of the smectic A (S_A) in the classification of liquid crystal because any splitting of the diffractions on the meridian and equatorial lines is not observed.[19] Accordingly, bundles of mesogenic groups form stacked layers and the planes of the each layer are arranged perpendicular to the stretched direction without tilting. Thus the quenched PBN has a structure of S_A, but the fluidity is frozen. A solid phase having a liquid crystalline structure, which is termed "liquid crystal glass" (LC glass), is reported.[20] It should be noted that the reported LC glass is obtained by cooling a liquid crystal and is apt to co-occur with crystal because the crystal phase is located below the liquid crystal phase,[20] whereas the relevant structure of PBN is formed at a temperature below the crystal phase like in the case of the mesomorphic iPP.[13] Hereinafter, we refer to such a solid form of PBN as the "mesomorphic" phase of PBN.

Incidentally, the smectic period of the mesomorphic phase of PBN is a very similar to the fiber period of the α-form crystal rather than that of the β-form; the length of a unit cell in *c*-axis for the α- and β-forms are 14.36 Å and 15.4 Å, respectively.[1] Therefore, it is considered that the local chain conformation of PBN in the mesomorphic phase is the same as that in the α-form crystal and that the peak at $q = 0.44$ Å^{-1} in the WAXD is assigned to the (0 0 1) plane of the S_A.

3.2. Annealing of Quenched PBN. Figure 3 shows 1D-WAXD of the (nonstretched) mesomorphic PBN during a heating process. The sharp peak at $q = 0.44$ Å^{-1}, the characteristic of the mesomorphic phase, becomes week above 70 °C and eventually disappears. On the other hand, the α-crystal peaks[1] at $q = 0.58$, 1.04, 1.09, 1.40, 1.57, 1.70, 1.83, and 2.02 Å^{-1} appear above the corresponding temperature. This result shows that the mesomorphic phase transforms into α-crystal above ca. 70 °C. It should be noted that the α-form crystal is preferentially obtained by heating up from the mesomorphic phase. This is probably because the local chain conformation of PBN in the mesomorphic phase is the same as that in the α-form crystal as was mentioned in the previous section. When the PBN was heated further, the β-crystal peaks[1,2] at $q = 0.92$, 1.20 and 1.84 Å^{-1} appear above 180 °C. All crystalline peaks disappear at 246 °C and a single broad peak remains.

Figure 4 shows the temperature dependences of $I(q)$ at $q = 0.44$ Å^{-1}, the (0 0 1) plane of the mesomorphic phase, and $I(q)$ at $q = 0.58$ Å^{-1}, the (0 0 1) plane of the α-crystal. It is apparent that above 70 °C the former decreases and the later increases, corresponding to the mesomorphic to α-crystal transition. It is

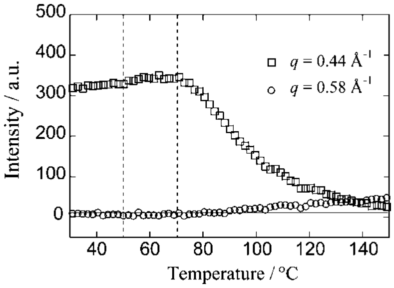

Figure 4. Temperature dependence of $I(q)$s at $q = 0.44$ Å^{-1} (open circles) and $q = 0.58$ Å^{-1} (open squares).

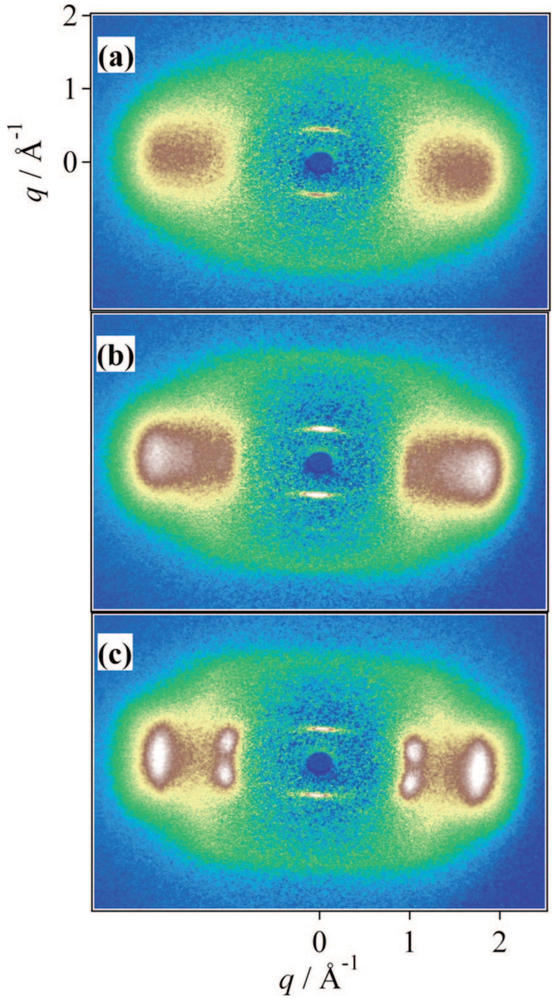

Figure 5. 2-dimensional WAXD images of a four-times stretched specimen of the quenched PBN during a heating process at 50 (a), 70 (b), and 100 °C (c).

also apparent that below 70 °C the $I(q)$ of the mesomorphic phase increases, however, if one examines minutely, the increasing rates above 50 °C seems to be slightly higher. This delicate behavior is more clearly seen for the stretched specimen as described below.

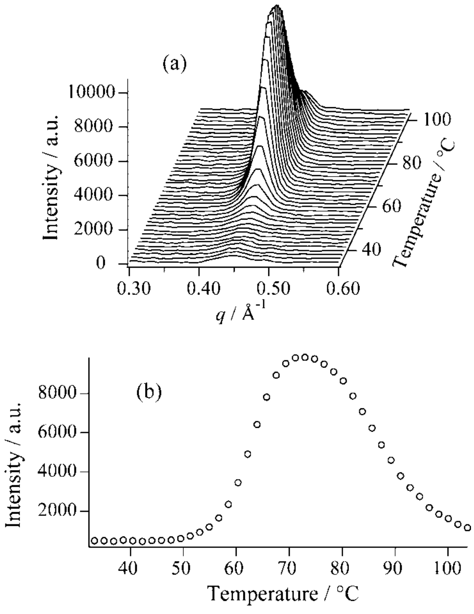

Figure 6. (a) Sliced profiles of 2-dimensional WAXD images (Figures 5) on the meridional direction. (b) Temperature dependence of $I(q)$ at $q = 0.44$ Å^{-1} in part a.

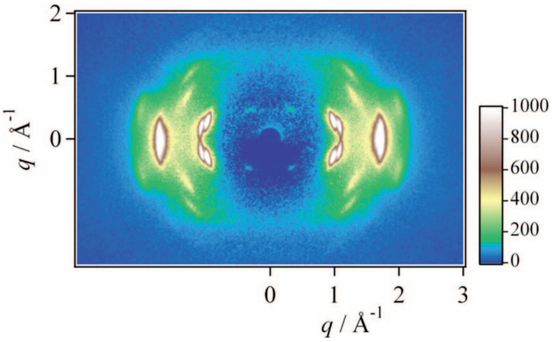

Figure 7. 2-Dimensional WAXD image for the stretched mesomorphic PBN at 200 °C.

2D-WAXD images of a four-times stretched PBN at 50, 70, and 100 °C during a heating process with a heating rate 4 °C/min are shown in Figure 5, parts a, b, and c, respectively. The intensity of the (0 0 1) peak for the mesomorphic phase is the highest at 70 °C (Figure 5b) among three. This result suggests the characteristic of the mesomorphic phase becomes the strongest at around 70 °C. Two broad peaks at around $q = 1.4$ Å^{-1} on the equatorial direction at 50 °C (Figure 5a) split into four broad peaks on the equatorial direction at 70 °C; the inner peaks at around $q = 1.0$ Å^{-1} and the outer peaks at around $q = 1.8$ Å^{-1} (Figure 5b). Then, the inner broad peaks split into four spots on the meridian at 100 °C (Figure 5c). The four strong inner peaks are assigned to the combination of (0 1 0) and (0 $\bar{1}$ 1) planes of α-form,[1] and the tilting of the crystalline unit causes this split.

Figure 6a shows the sliced intensity profiles along the prime meridian of 2D-WAXD (Figure 5) as functions of q and temperature. Figure 6b shows the temperature dependence of $I(q)$ at $q = 0.44$ Å^{-1} (mesomorphic peak) in Figure 6a. The mesomorphic peak intensity remains below 50 °C, and increases between 50 and 70 °C, and then decreases above 70 °C. Namely, the behavior described for the nonstretched specimen (Figure 4) is enhanced for the stretched specimen (Figure 5c). These results suggest that the residual amorphous, which was formed in the quenching process, transforms into mesomorphic phase between 50 and 70 °C, and the mesomorphic phase transforms into α-crystal above 70 °C.

Figure 7 shows the 2D-WAXD image of the stretched specimen at 200 °C. Figure 7 does not show two strong peaks on the prime meridian any more, but the peaks split into four weak spots on a latitude line. This result indicates that the naphthalene parts, which play a role of mesogen in the mesomorphic (S_A) phase, tilt during the crystallization.

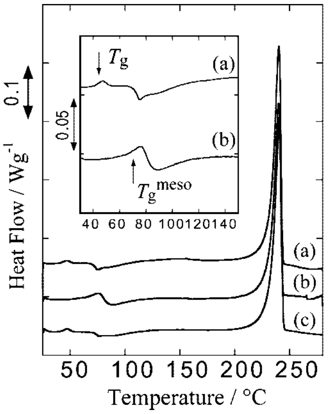

Figure 8. DSC curves of heating process for nonstretched PBNs: (a) as quenched specimen; (b) Annealed at 70 °C for 30 min after quenching; (c) vacuum-dried for 2 days, where the heating rate for both cases is 4 °C/min. The inserted figures are enlarged curves of parts a and b for a range between 25 and 150 °C.

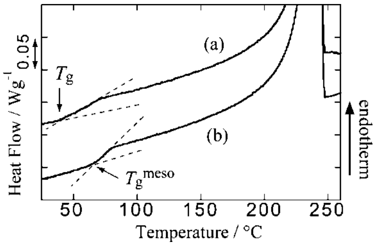

Figure 9. Reversing heat flows obtained by TMDSC of heating process for nonstretched PBNs: (a) as quenched specimen; (b) specimen annealed at 70 °C for 30 min after quenching. Heating rate for both the cases is 1 °C/min.

3.3. Glass Transition Temperature of Mesomorphic Phase. DSC curves a, b, and c in Figure 8 show the heating processes for the PBN as quenched, for the quenched PBN annealed at 70 °C for 30 min then requenched and for the quenched PBN vacuum-dried for 2 days, respectively. Curve a shows an endothermal peak at 47 °C, an exothermal peak at 75 °C, an exothermal broad shoulder at around 90 °C and a distinct endothermal peak at 240 °C. Curve b shows an endothermal peak at 75 °C, an exothermal broad peak at 90 °C, and an endothermal peak at 240 °C. It is unquestionable to assign the distinct endothermic peak at 240 °C observed in both curves a and b to the melting of the crystal by considering the results of WAXD in the heating process (Figure 3).

Meanwhile, it should be argued on the assignment of the other peaks. As was referred to in Introduction, variety of values for the glass transition temperature T_g of PBN have ever been reported, such as $T_g = 41$,[7] 48,[8] 52,[9] 66,[10] 71,[11] and 82 °C.[12] The diversity of the values is probably due to the thermal history of the samples. First, to eliminate uncertainties in the date due to the residual water, which might be absorbed during the quenching process, a specimen vacuum-dried for 2 days after quenching was also measured. The resulting DSC curve c for the dried PBN specimen is essentially the same as that of the nondried one (part a) in Figure 8. Therefore, the multiple peaks observed in Figure 8 have nothing to do with the water.

Next, in order to extract bare glass transition behavior from the complicated endo and exothermal peaks, the storage parts of the heat flows, i.e., reversing heat flows[21] were measured using TMDSC for the PBN specimens. The TMDSC curves for the PBN as quenched (a) and for the PBN annealed at 70 °C for 30 min after quenching (b) are shown in Figure 9. The glass transition temperatures for the PBN as quenched (a) and for the PBN annealed at 70 °C for 30 min after quenching (b) are 41 and 65 °C, respectively, by taking the onset temperatures of the heat capacity shift. As was shown in Figures 4 and 6, the characteristic of mesomorphic phase (q = 0.44 Å^{-1}) is enhanced above 50 °C. Therefore, we consider the glass transition temperatures 41 °C observed for the PBN as quenched (a) and 65 °C observed for the PBN annealed at 70 °C for 30 min after quenching (b) as that of the amorphous (T_g) and that of the mesomorphic phase (T_g^{meso}), respectively.

With the help of the results by TMDSC, the complicated behavior in Figure 8 is mostly solved as follows. The endothermal peaks at 47 °C (Figure 8a) and 75 °C (Figure 8b) are attributable to the grass transition phenomena of the amorphous and the mesomorphic phase, respectively. The broad exothermal shoulder (Figure 8a) and peak (Figure 8b) at around 90 °C are attributable to the crystallization by considering the results of WAXD in the heating process (Figure 3).

The remaining problem is the interpretation for the "exothermal" peak at 75 °C (Figure 8a). At this moment, we assume the peak is due to the transition from the amorphous to the mesomorphic phase. One reason is that the annealed specimen (Figure 8b), in which the remaining amorphous part has already been transformed into the mesomorphic phase during the annealing, does not show this "exothermal" peak. Furthermore, the characteristic of the mesomorphic is enhanced toward 75 °C, judging from Figure 6b.

After all, the PBN has two glass transition temperatures, i.e., the glass transition temperatures of normal isotropic glass (T_g) at 41 °C and the glass transition temperature of the mesomorphic phase (T_g^{meso}) at 65 °C. The latter is located in the higher temperature than the former ($T_g^{meso} > T_g$). Multiple glass transition behavior has been reported also for the system of liquid crystalline polymers that yield the LC glass, where the glass transition temperature of the LC glass (T_g^{LC}) is located in the lower temperature than the normal T_g ($T_g^{LC} < T_g$).[20,22–26] Although the mesomorphic PBN and the LC glass have similar characteristic solid structure, the relationship of relative temperatures between the normal T_g and the additional glass transition temperatures associated with these characteristic solid structures are inverted. The relativity of T_g^{LC} andT_g^{meso} to T_g probably correlates closely with the temperature phase diagram whether such characteristic solid structures are formed below or above the crystal phase. Watanabe[20,22] explained that the T_g of liquid crystal (T_g^{LC}) is lower than the normal T_g using a mode coupling theory to hard ellipsoids.[27] According to this theory, the ellipsoids with aspect ratio greater than a critical value 2.5 freeze their orientational degree of freedom and enhance the fluidity. However, the target of this liquid crystal theory is nematic phase rather than smectic phase. The smectic phase has not only orientational order but also one-dimensional positional order. When the later order strongly affects the molecular motions, a mobility of smectic phase might be slower than that of isotropic liquid, and thus T_g of smectic phase also might be higher than that of isotropic liquid. Chen and Zackmann[23] pointed out a possibility that the T_g^{LC} is higher than T_g ($T_g^{LC} > T_g$) with free volume theory. According to the explanation, the T_g^{LC} should be higher than the normal T_g when the difference between the volumes at T_g^{LC} and at the normal T_g is smaller than the volume change upon the liquid crystallization. From the discussion above-mentioned, the relation of two T_gs ($T_g^{meso} > T_g$) for PBN is not improbable.

4. Conclusion

It was found that the mesomorphic phase is formed when the molten PBN is quenched to 0 °C by dipping into ice–water. The structure of the mesomorphic phase was assigned to a smectic A structure. The local chain conformation in the mesomorphic phase is the same as that in the α-crystal.

Although the mesomorphic phase of PBN has a liquid-crystal-like structure, it is formed below the melting temperature of crystal. This point is different from the case of liquid crystal glass. The mesomorphic phase of PBN has a glass transition temperature T_g^{meso} at 65 °C besides the normal glass transition temperature T_g for the isotropic glass at 41 °C. The α-form crystal was preferentially obtained by the crystallization from the mesomorphic PBN.

Acknowledgment. The authors cordially thank Professor H. Tanaka at Institute of Industrial Science, The University of Tokyo, for his kind help in TMDSC measurements. This work was supported by KAKENHI (Grant-in-Aid for Scientific Research) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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