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Mesomorphic phase in oriented poly(pentamethylene 2,6-naphthalate)

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ABSTRACT

The mesomorphic structure of poly(pentamethylene 2,6-naphthalate) (PPN) was investigated using a synchrotron X-ray scattering. The PPN fibers cold-drawn from the super-cooled amorphous state showed a smectic mesomorphic structure and further a crystalline phase at high strain. Based on the experimental evidence showing the split of amorphous halo up and down the equator and the conformational constraint suggested by the crystal structure refinement and computation, we suggested the smectic phase as S_{CA} where the mesogens are tilted against the layer surface normal and the tile direction is opposite between the neighboring layers.

Polymer liquid crystals will most certainly become more important as research into this field progresses. Applications for these materials range from the production of high-strength materials to their use in electrical or optical devices. The polymer liquid crystal phase was first discovered in the solution of the tobacco mosaic virus, which is a rigid polymer a few hundred nanometers long [1]. Up to now, there have been so many reports about liquid crystalline polymers (LCP). Among these polymers aromatic polyester is the most well-known family. In most cases, they form smectic mesomorphic structure, which is associated with the mesogenic moieties (phenyl, biphenyl, or naphthalate) incorporated in the polymer backbone.

Two interesting features are noted with these polyester series. One is that their mesophase existence and transition behaviors are effected by the length of methylene spacer. Odd–even effect can be seen in poly(alkylene 4,4′-bibenzoate)s (BB-*n*, *n*: number of carbon in the methylene spacer) [2–6]. These BB-*n* polyesters invariably form smectic mesophase when *n* varies from 3 to 9. In BB-*n* with an even *n*, S_A phase is formed with both axes of the polymer chain and biphenyl mesogen lying perpendicular to the layers. In contrast, the smectic structure of BB-*n* with an odd *n* was identified as S_{CA} phase, in which the tilt direction of the mesogenic group is matching in every second layer but opposite between neighboring layers. Another interesting feature is that in some polyesters the mesomorphic phase is induced only by stretching the polymer in super-cooled amorphous state. Poly(ethylene terephthalate) (PET) is the most well-known example whose mesophase existence upon stretching have been extensively studied, initially by Bonart [7,8] and followed by Asano and Seto [9]. Several papers were reported in more recent years [10–13]. In our previous work, we also reported the existence of mesophase in cold-drawn PET fiber [13] and the physical properties associated with the presence of mesophase [14].

Polyester based on 2,6-naphthalene dicarboxylic acid, poly(*m*-methylene 2,6-naphthalate) (P*m*N, where *m* is the number of methylene unit) is another example of LCP that possibly show mesophase. In this family, as was noted in BB-*n* family, the macroscopic thermal and mechanical properties exhibit odd–even fluctuations as the number of methylene group in P*m*N increases [15]. However, the existence of mesophase in these polymers is relatively rare and has been reported only in PEN [16,17] and PBN [18], where PBN showed the S_A phase.

In this report, we present the mesophase structure in poly(pentamethylene 2,6-naphthalate) (PPN). The monomeric unit of PPN consists of the flexible part, pentamethylene, and the rigid part naphthalene [19]. This polymer shows very slow crystallization rate, which provides an easy control of the morphology during the induction period of crystallization [20]

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This characteristic is similar with the case of poly(ethylene terephthalate) (PET) but quite a contrast to the case of poly(butylene 2,6-naphthalate) (PBN) within their group.

In order to examine the existence of mesophase and related structure in PPN, quenched amorphous samples were cold-drawn (2 mm/min) to various strains at room temperature. For the structural investigation we utilized the synchrotron X-ray scattering facility at Pohang Accelerator Laboratory (PAL) in S. Korea. During the measurement the length of specimen was fixed in order to prevent the thermal shrinkage. Some of two-dimensional WAXD patterns of cold-drawn PPN sample measured at room temperature and upon raising temperature (3°C/min) are shown in Fig. 1(a) and (b), respectively. From the WAXD pattern at room temperature (Fig. 1(a)), the structure of PPN sample at strain 4 clearly shows the strain-induced crystallization. However, drawn samples (strain = 1–3), exhibit two weak but sharp peaks at low angles in the meridian and two broad peaks at high angles in the equator. The sharp peak observed in the meridian implies a certain longitudinal order in the drawn PPN, similar to the fiber period in crystalline structure. On the other hand, the broad halo in the equator suggests the absence of long range order between the drawn PPN chains. These results suggest that the drawn PPN has certain low dimensional order, namely the mesophase, which resembles smectic LC order as has been observed in the oriented polymers having the flexible spacers between the rigid units [2–7,9–13,16–18].

Fig. 1(b) shows X-ray patterns of oriented PPN (strain = 2) measured during the heating process. Upon increasing the temperature, the diffused pattern becomes highly crystalline, indicative of representative triclinic crystal structure development. Simultaneously, a sharp two-point diffraction at $2\theta = \sim 6^\circ$ in the meridian becomes four-point pattern. Here, we only focus on the mesophase structure of PPN before the onset of crystallization. The meridional and lateral slices shown in Fig. 2(a) and (b) display that the sharp and laterally diffused peak begins to intensify and focus into a point shape when the temperature reaches ~48 °C and maximizes at ~55 °C. We note that the T_g of PPN is about 48 °C [15]. Increasing the temperature further, however, the intensity of meridional peak becomes weak and laterally diffused again and then splits into a four-point pattern (Fig. 2(b)), demonstrating the tilting of layer surface during the crystallization. This observation provides an important clue suggesting how the chains are rearranged to form crystalline structure from the mesophase. The split of meridional peak occurs quite fast and clear. Around 59 °C near-meridional four-point pattern becomes discernible and the split seems to complete at 72 °C. The four-point pattern, which assumed to be (002) reflection, stabilizes above 72 °C and the angle between this (002) reflection and meridional direction maintains constant with the further increase of temperature. The initial two-point meridional diffraction, on the other hand, can be associated with the transient structure prior to the triclinic crystal lattice formation. The d-spacing of the meridional peak, i.e. the smectic layer thickness derived from the peak position is plotted in Fig. 3. It is shown that the d-spacing increases with the increase of strain (Fig. 3(a)) but remains constant with the increase of temperature as far as the temperature is below T_g (Fig. 3(b)).

In the polymeric smectic phase, each mesogenic group participates in each layer, and so the polymer molecule must adopt a conformation or packing which is compatible with the smectic layer thickness. The peak location and profile along the meridian and the transverse direction (Fig. 2(a) and (b)) suggest that the diffraction is arising from the ordering of the mesogenic groups both in the direction of fiber axis and in the transverse direction across the chain bundles, where individual assembly of the mesogenic groups across the chain bundles resembles a layered structure with the horizontal surface. The initial two-point meridional reflection suggests that the planes of each mesogenic layer arranged perpendicular to the stretched direction.

Now we attempt to classify the smectic mesophase. The classification depends on both aligned direction of mesogenic group and polymer chain against the fiber axis. First, we begin with our experimental observation that the equatorial broad halo from the mesophase is splitting up and down the equator (Fig. 2(c)). The results are evidently suggesting the tilted mesogens against the fiber axis. The tilt angles estimated from the XRD pattern show slight increment with the temperature but remain unchanged with the increase of strain. It is elucidated that the tilt angle ranges 14°–17° and reaches maximum of 19° at early stage of crystallization. However, it is not definitive whether the smectic phase is S_C or S_{CA} where the mesogens are

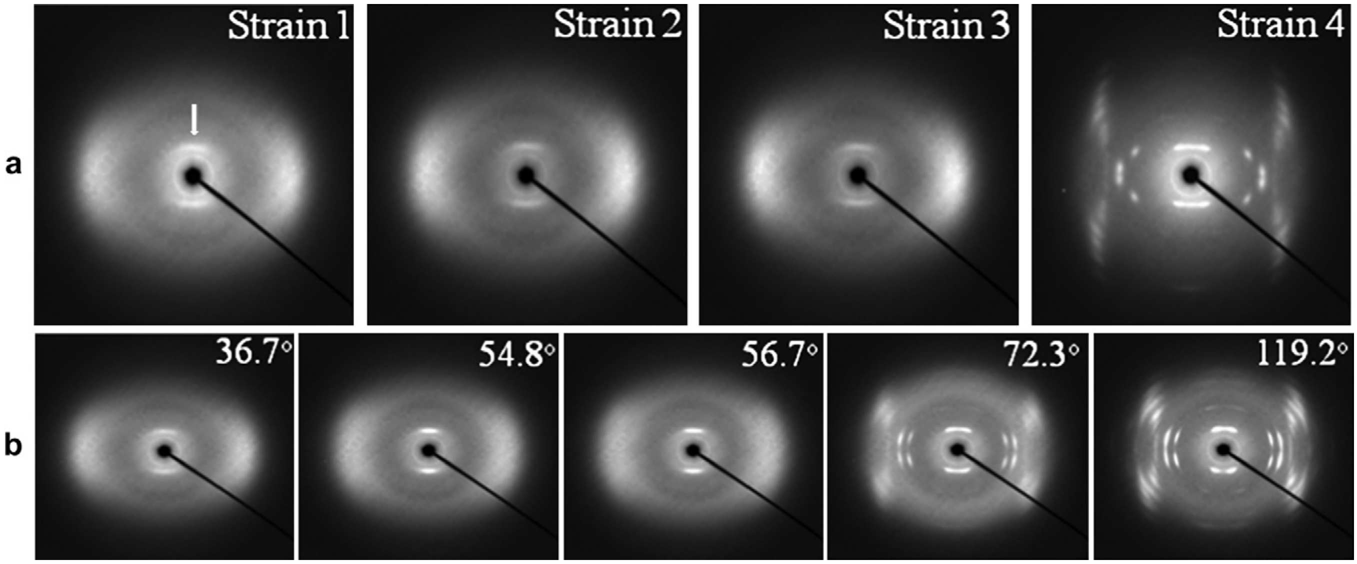

Fig. 1. Wide-angle X-ray diffraction patterns of cold-drawn PPN samples; (a) different strains, measured at room temperature, (b) measured at elevated temperatures for the strain = 2. The stretched direction is parallel to the meridional direction in the images. The ring-shaped weak reflection appeared around the beam stopper is from the imide film attached outside the block holder.

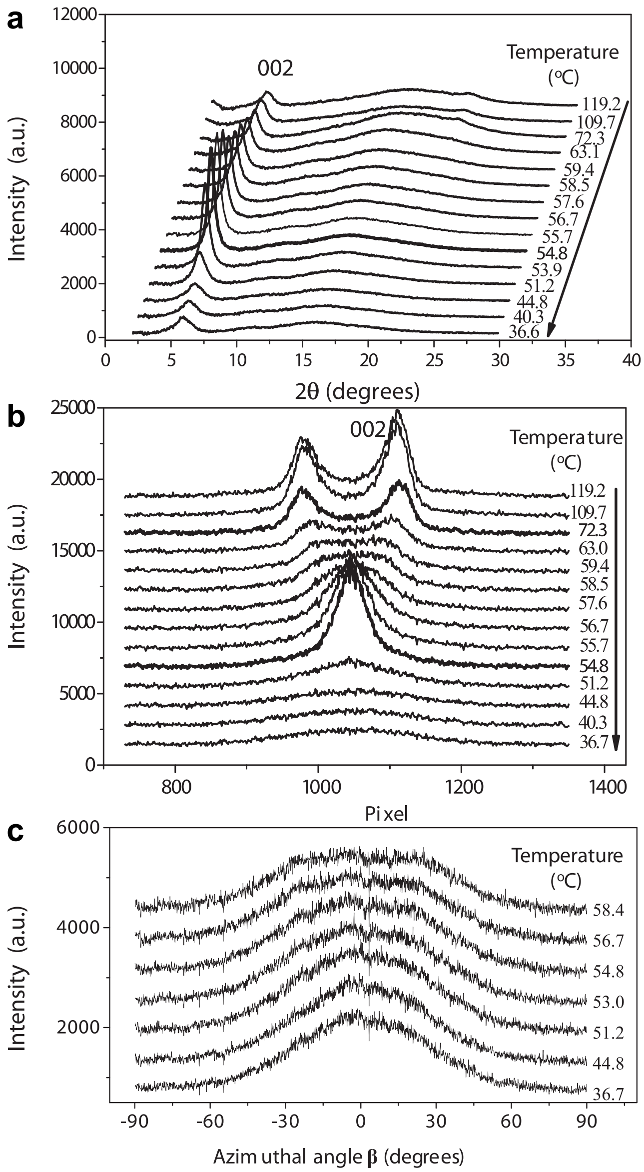

Fig. 2. Intensity profiles of meridonal peak obtained from X-ray patterns in Fig. 1(b); (a) along the meridian, (b) along the horizontal line, and (c) azimuthal intensity distribution of the broad equatorial reflection at $2\theta = 20.1°$.

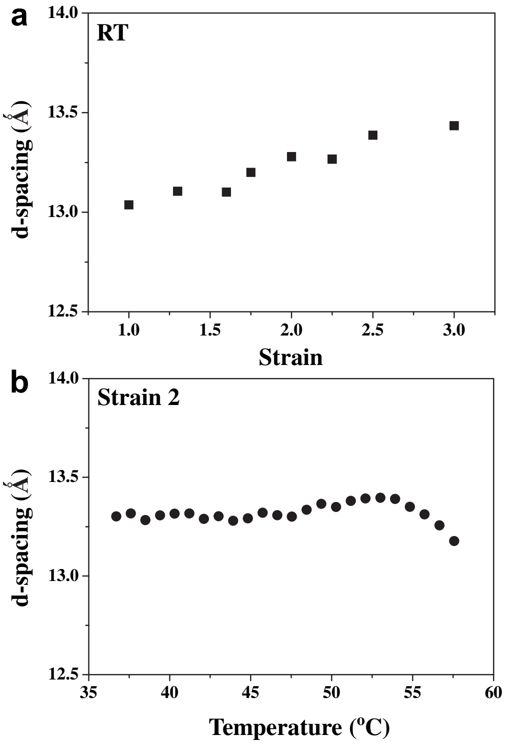

Fig. 3. d-Spacing change of meridonal peak vs. strain (a) and temperature (b). Plot (b) is for the PPN of strain = 2.

tilted anti-clinically as has been observed in other odd-numbered polyesters. As described before, the odd–even effects in polyesters are commonly seen not only in mechanical or physical properties but also in crystal and mesomorphic structure. In odd-numbered methylene spacer polymers, the mesogenic groups are alternatively tilted toward each other which is caused by the conformational constraint [3,6,21]. The conformation analysis of odd–even effect in polyester mesophase was also performed by Abe [22]. Abe's computational analysis demonstrated that the mesogens of odd-numbered polymer are inevitably tilted with each other. Recent report on PPN crystal structure refinement [19] or the energy minimized conformation (Fig. 4(a)) indeed confirm the anti-clinically inclined mesogens. Based on the experimental results and the conformation suggested by the crystal structure as well as the computer simulation, it is quite reasonable to assume that the mesogenic units are anti-clinically tilted in the mesomorphic state as depicted in Fig. 4(b), therefore, the S_{CA} phase. The observed layer thickness (13.04–13.50 Å) is quite shorter than the fiber period (14.58 Å) estimated from the crystal structure or the computer simulation. However, this can be reasonably explained by the orientational disorder of the mesogens and spacer within the smectic layer. According to the diffuse cone model as suggested by de Vries et al. [23] the difference between the observed and calculated values in layer spacing can be attributed to the average tilting of molecules

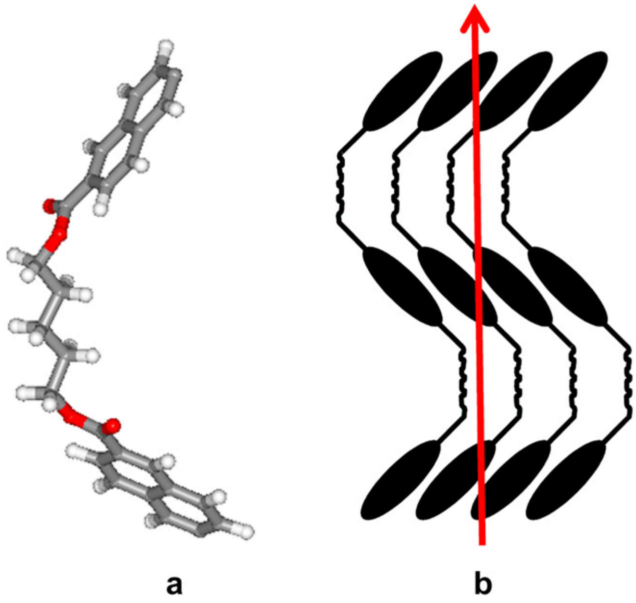

Fig. 4. Energy minimized conformation of PPN chain units by Cerius^2 program (a) and suggested arrangement of mesogens and spacers in a smectic CA layer structure (b). The arrow indicates the molecular axis of PPN. The scribble in spacer indicates unidentified conformation in spacer.

against the layer normal which is caused by the orientational disorder. For an orientational order parameter $S = 0.8$ as usually observed for the low molar mass S_A, the diffuse cone model gives an averaged value of $⟦\cos\theta⟦ = 0.927$. Applying this for the present PPN, we calculate the spacing $d = 13.52$ Å. This value is very close to that of the PPN of (strain = 3). It is also expected that the spacer molecules may adopt an appreciable amount of the gauche conformer so as to reduce the layer thickness further.

In summary, we reported for the first time that the cold-drawn PPN showed an intermediate mesomorphic phase. We propose the mesophase is S_{CA} where the overall molecular axes is perpendicular to layer surface but mesogens are tilted with the tilt direction being opposite between the neighboring layers. Detailed studies on the mesophase and the structure evolution from the mesophase are now underway.

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