Thermotropic Liquid Crystals of Main-Chain Polyesters Having a Mesogenic 4,4′-Biphenyldicarboxylate Unit. 13. Characteristic Deformation of Smectic Layer Structure Induced by Elongation of Uniaxially Oriented Fiber Composed of Smectic CA Glass

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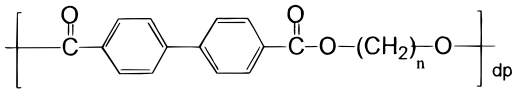
ABSTRACT: Elongation deformation of the smectic layer structure was examined by mechanical and X-ray measurements for the oriented fiber of the main-chain BB-5 polyester. In this oriented fiber, a smectic CA (SmCA) structure is solidified with the mesogenic groups arranged in a zigzag fashion and with the layers aligned perpendicular to the fiber axis. The fiber could be elongated at room temperature until the strain of around 20%. On elongation, the polymer chain was stretched and succeedingly relaxed to recover the initial zigzag conformation. The relaxation was followed by the characteristic undulation of smectic layers.

Introduction

In this series of studies,[1−10] we have treated the following main-chain LC polyesters designated as BB-*n*, where *n* is the carbon number of the methylene spacer.



These BB-*n* polyesters form smectic mesophases when *n* varies from 3 to 9. Interesting is that the different types of smectic phases are formed between BB-*n* polyesters with even and odd *n*. In BB-*n* with an even *n*, the smectic A (SmA) phase is formed with both axes of the polymer chain and biphenyl mesogen lying perpendicular to the layers.[1,2] In contrast, the smectic structure of BB-*n* with an odd *n* was identified as the smectic CA (SmCA), in which a tilt direction of the mesogenic group is same in every second layer but opposite between neighboring layers.[1−3] This distinct difference in the basic smectic structure between odd and even series is caused by a conformational constraint of the alkylene spacer.[10]

For a detailed examination of the structures and properties of the mesophases, it is necessary to prepare the monodomain or uniaxially oriented smectic phase. In the polymeric system, the most convenient way is to draw the fiber. There are two melt phases that are available to draw the fiber in the BB-*n* polyester system. One is an isotropic melt, and the other is a smectic melt.[2,8] It is noteworthy that the fibers drawn from these two phases show entirely different molecular alignment. In the fiber drawn from the isotropic melt, the polymer chains arrange parallel to the fiber axis as observed in conventional polymer fibers. On the other hand, for the fibers drawn from the smectic melt, the polymer chains lie perpendicular to the fiber axis. This anomalous orientation is explained to be resulted from the mutual slip of the chain folded lamellar domains.[11] By using these highly oriented fiber specimens, the SmA, SmCA (or chiral SmCA), and SmC (or chiral SmC) phases have been successfully identified in the main-chain BB-*n* polyesters.[2−7,10]

In this study, we examined a deformation of smectic layer structure by an elongation of the fiber, focusing on the characteristic SmCA structure of BB-5. The uniaxially oriented fiber with the structure of the SmCA glassy state was elongated at room temperature (20 °C). Interestingly, the elongation resulted in the undulation of smectic layer as a consequence of relaxation from the stretched chain conformation. Internal deformation by elongation and structural change through relaxation process were investigated with the mechanical and X-ray measurements.

Experimental Section

BB-5 polyester was synthesized by melt transesterification from dimethyl *p*,*p*′-bibenzoate and pentanediol with isopropyl titanate as a catalyst.[1] The inherent viscosity is 0.82 dL/g as measured at 30 °C by using 0.5 g/dL solution in 60/40 w/w mixture of phenol and tetrachloroethane. Transition temperatures as measured at a normal scanning speed of 10 °C/min are shown below.

$$\text{crystal} \underset{86\ ^\circ\text{C}}{\overset{173\ ^\circ\text{C}}{\rightleftharpoons}} \text{smectic CA} \underset{196\ ^\circ\text{C}}{\overset{212\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic}$$

X-ray diffraction patterns were performed using a Rigaku-Denki RU-200 BH with Ni-filtered Cu Kα radiation. Stress−strain and stress−relaxation curves were obtained at 20 °C by Seiko Instruments TMA SSC5200.

Results and Discussion

Figure 1a shows the X-ray photograph of BB-5 fiber taken at room temperature. Here, the fiber was spun from the isotropic melt, annealed at the SmCA temperature around 180 °C for 10 min, and then quenched to room temperature. The pattern is the same as observed at the SmCA temperature, indicating that the SmCA phase is glassified.[9] The glass transition temperature was elucidated as around 50 °C with both DSC and

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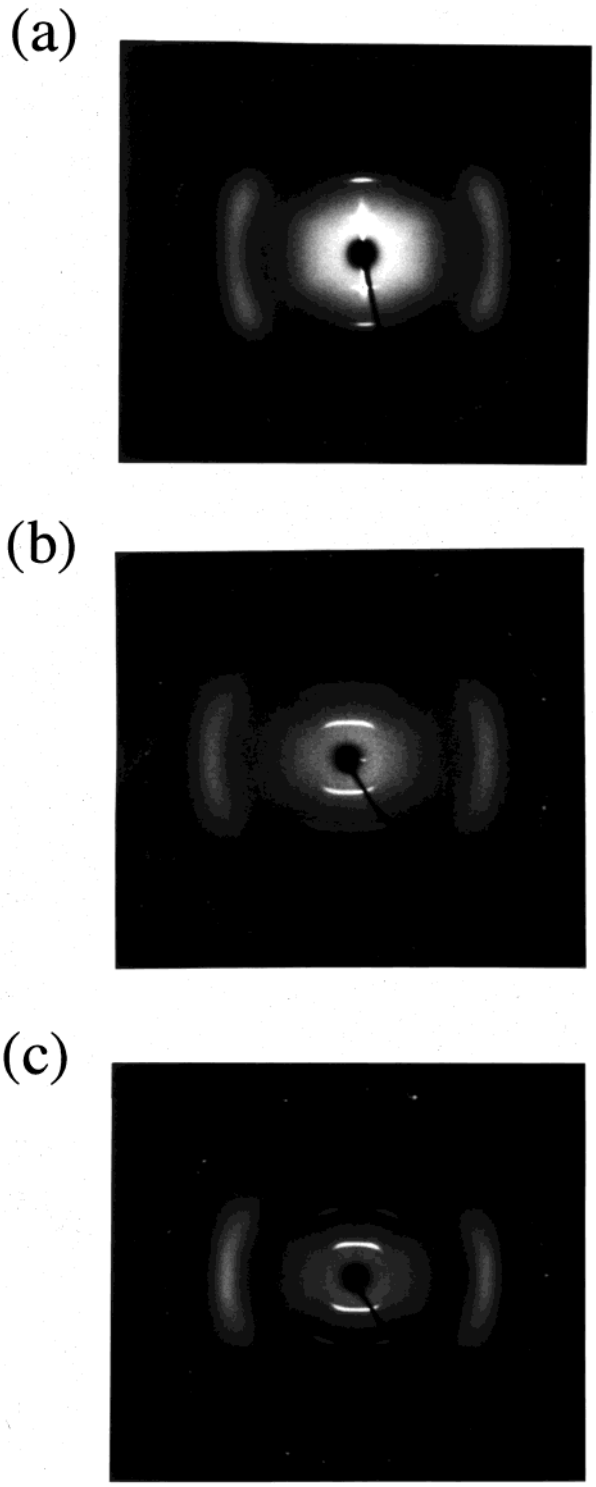

Figure 1. X-ray photographs observed for the BB-5 fiber: (a) spun from the isotropic melt and (b) elongated with a strain of 15% at a temperature of 20 °C for 5 min and (c) for 200 h. The fiber axis is in a vertical direction.

dynamic mechanical measurements.[9] In Figure 1a, the sharp layer reflections are observed on the meridian and the broad reflections at positions above and below the equator. These are characteristic of the SmCA structure.[2,3] Figure 2a illustrates the molecular orientation, as has been determined from the X-ray pattern and optical properties.[2,3] The polymer chains with the zigzag alignment of the biphenyl mesogens orient parallel to the fiber axis and the smectic layers lie perpendicular to it.

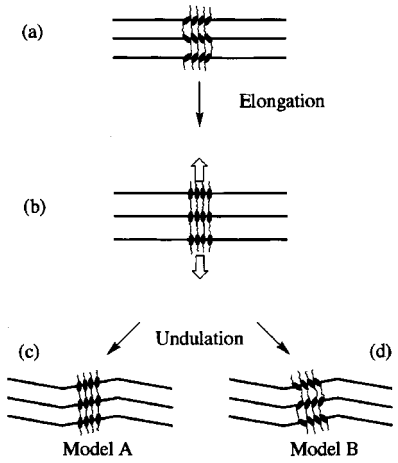

Figure 2. Tentative illustration of structural change in the glassy SmCA LC under an elongation of the BB-5 fiber: (a) the original structure, where the mesogenic groups are tilted in an alternate fashion to the fiber axis, (b) the structure formed just after the elongation, where the polymer chain stretches and the mesogens lie parallel to the fiber axis, and (c) and (d) are possible relaxed structure based on the X-ray pattern shown in Figure 1c. Model A shown in (c) is the same with SmC structure of BB-*n* polyesters. Model B shown in (d) is the SmCA structure with layer undulation. The fiber axis is in a vertical direction.

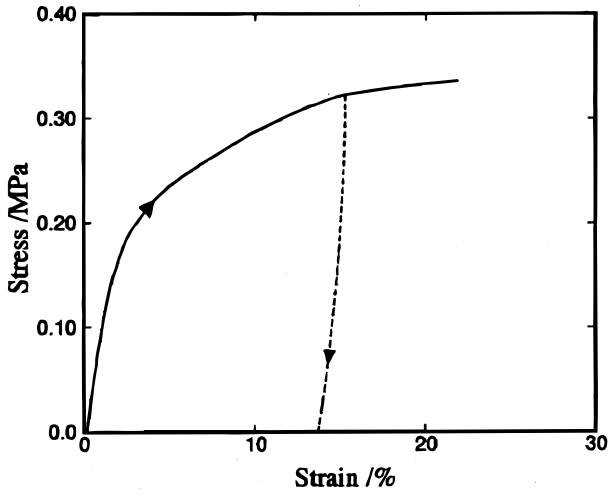

Figure 3. Stress−strain curve for the BB-5 fiber. Solid curve was observed up to the breaking point around 20%, and dashed line is the relaxation curve on unloading at the strain of 15%.

What happens on stretching such a glassy SmCA fiber? Since the mesogenic groups are tilted in an alternate fashion to the layer normal, one can suppose that the polymer chain may be extended so that the neighboring mesogenic groups within a chain are parallel to each other like in the SmA structure of even series of polymers[12] (compare parts a and b of Figure 2). The layer spacing of the resulting SmA should be 17.2 Å, which is a simple average of 15.8 Å for the layer spacing of the SmA in the BB-4 and 18.4 Å for that in the BB-6.[1,10] Then, the minimum extension of around 10% is expected since the layer spacing in the SmCA of the BB-5 is 15.4 Å.

The stress−strain curve is given in Figure 3. Here, the fiber in a length of 5 mm was elongated at room temperature with a constant rate of 0.25 mm/min. At low strains (∼3%), the stress shows a steady increment with apparent modulus (i.e., slope) of 0.6 GPa. An elastic deformation is observed only in this low-strain region.

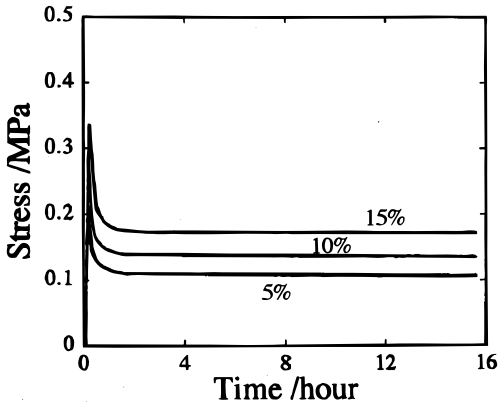

Figure 4. Stress−relaxation curve for the BB-5 fiber at a temperature of 20 °C. The applied strains are 5, 10, and 15%.

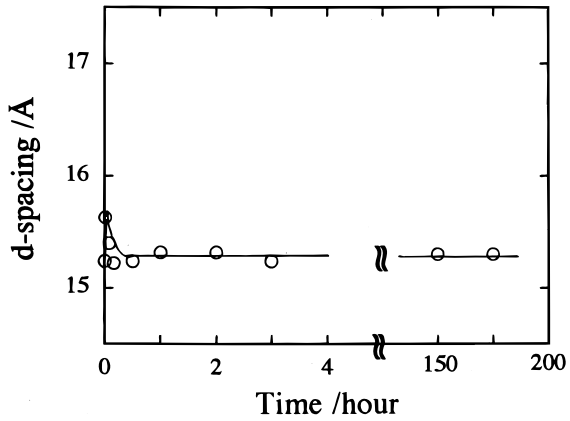

Figure 5. Time dependence of the smectic layer spacing of BB-5 under elongation with a strain of 15%.

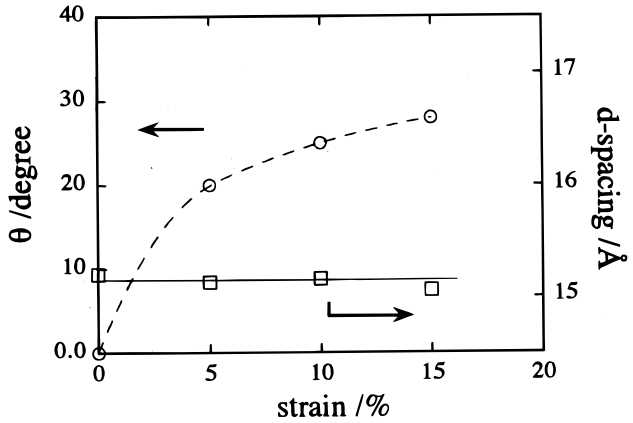

Figure 6. Variation of splitting angle of layer reflection, θ, and layer spacing, d_{001}, upon the strain of the BB-5 fiber. The values were collected for the sample elongated for 200 h.

By further elongation, the slope decreases and the stress reaches steady value. Breaking occurs after the large strain around 20%.

As expected from the characteristic stress−strain curve, unloading in the strain region of 5%−20% before breaking of the fiber left almost its strain (see the dashed curve in Figure 3). This shows that the strain applied results in permanent deformation. However, the unloaded fiber can recover the original length when it is heated to the SmCA temperature. Thus, the elongation in this region includes neither chain breaking nor significant mutual slippage of molecules, but some specific deformation of which the initial structure can completely be recovered at a fluid liquid crystal state.

Figure 4 depicts the stress relaxation curves for the BB-5 crystals under various strains. The fibers were first elongated up to the strains of 5, 10, and 15%, and then the relaxation of stress was plotted against time with fixing the length. The stress decreases immediately after the elongation and reaches some value although a slight decrement continues over 15 h. Roughly a half value of initial stress is finally dissipated, suggesting that some significant structural change occurs under the stretch.

Internal deformation by stretching and structural change through the relaxation process were investigated by X-ray measurement. Figure 1b is the X-ray diffraction pattern of the fiber stretched for 5 min with a strain of 15%. Comparing with the original pattern of Figure 1a, it can seen that the layer reflections at small angle region is fairly spread out. After several days, they split into four spots, and the outer broad halos are centered around an equator as shown in Figure 1c. Thus, it is obvious that the smectic layer tilts with respect to the fiber axis similar to the SmC structure.[7] Figure 5 shows the variation of the layer spacing during the relaxation. The *d*-spacing increases immediately after 15% elongation and then decreases to a constant value for several days. A similar trend was observed for the fibers with 5% and 10% elongation. The splitting angles (θ) and layer spacing (d_{001}) collected after the relaxation for 200 h are plotted against a degree of elongation in Figure 6. The angle, θ, increases with a degree of elongation while the layer spacing remains constant around 15.2 Å which is approximate to the layer spacing of the original fiber. We thus conclude that the smectic layer expands momentarily but recovers its original layer spacing and that during this process the layer is tilted. Unloading does not affect the structure at all, but all of the fibers perfectly recover the original pattern of Figure 1a once they are heated to the SmCA temperature.

We consider some specific deformation which can conserve the applied energy or can dissipate the applied stress. It can easily be understood that at an initial stage of the deformation the zigzag conformation of polymer in the SmCA is stretched as illustrated in Figure 2b. The question is how the molecules rearrange to reach the final structure with the tilting of layers. Two processes are possible. As illustrated in Figure 2c,d, one is just like the SmC structure and the other is the SmCA structure with an undulation of layers. In the former case (model A of Figure 2c), the SmCA to SmC transition takes place on elongation and the tilting of layers in the SmC is caused by the mutual displacement of molecules. This type of tilting in the uniaxial fiber, in fact, has been observed for the BB-*n* polyester which exhibits the polymorphism of the SmA and SmC.[7,10] In this case, however, no dissipation of the applied stress is included, which is in conflict with the data of Figure 4. According to this point, the model B of Figure 2d is plausible. In this case, the extended conformation is relaxed to the initial zigzag conformation to dissipate the stress. At that time, the dimension parallel to the layer should be expanded since the repeat distance of polymer decreases. With maintaining the fiber dimension, such a conformational change can be allowed only by the undulation of layers[13] which takes place along the tilt direction of mesogenic groups (see Figure 2d). In the model B, the outer halos attributed to the

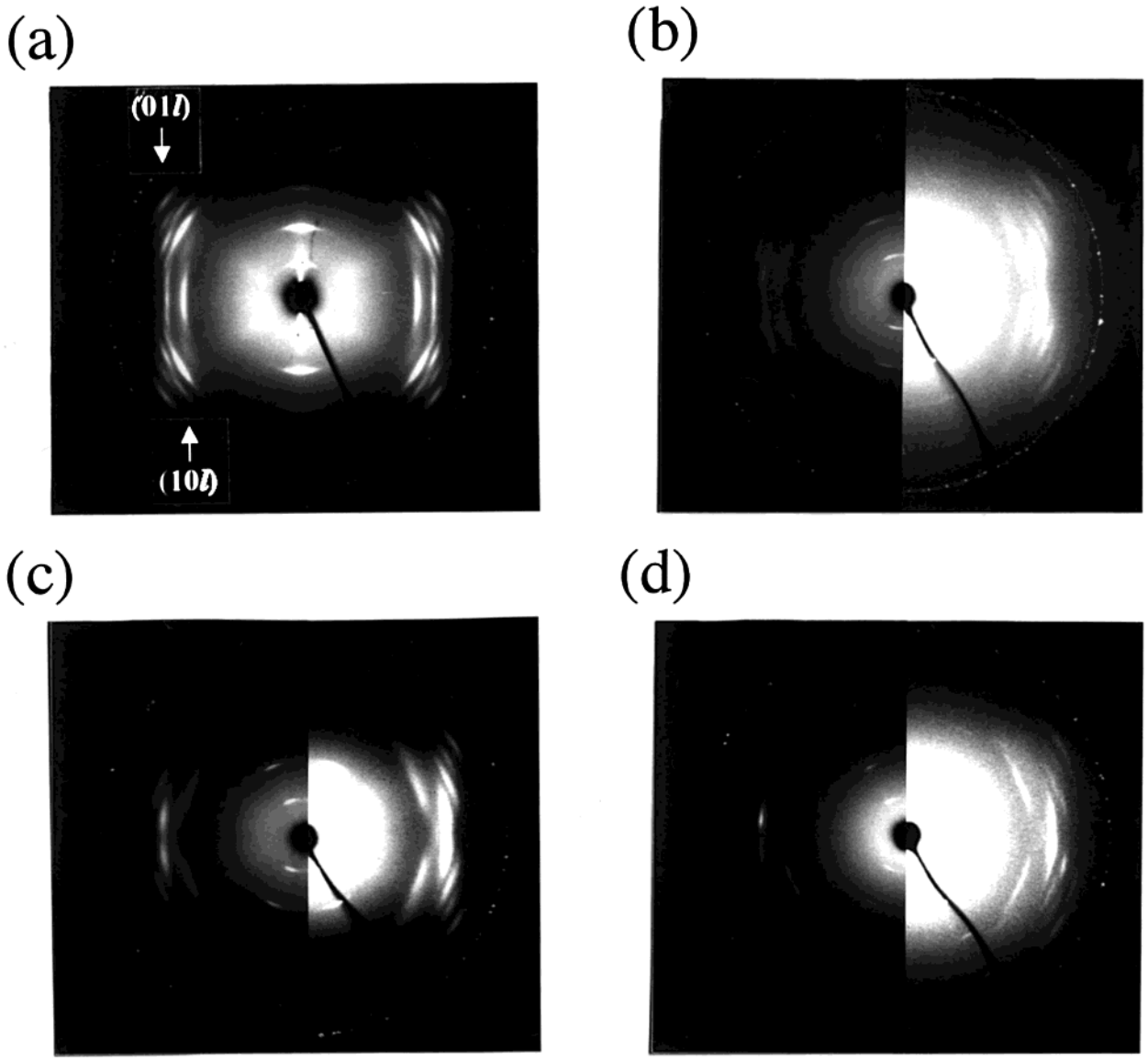

Figure 7. X-ray pattern of the BB-5 fiber crystallized under elongation with strain of (a) 0% (without elongation), (b) 5%, (c) 10%, and (d) 15%. The left-hand and right-hand side sections of pattern were taken with the different exposure time. The fiber axis is in a vertical direction.

disordered lateral packing of mesogenic group within a layer should appear both near meridian and near equator, but only one reflection on the equator is observed in Figure 1c. The halo appearing on the equator is attributed to the mesogens tilting with a smaller angle with respect to the fiber axis. The tilt angle of the mesogens is so small that the diffraction halo does not split but broaden in the azimuthal direction. The reflection for the mesogens tilting with a larger angle should be observed in the direction of the meridian. It is, however, not observed. It may be associated with the diffraction condition represented graphically with Ewald formation. The diffraction does not occur, and the halo is not observed in the X-ray pattern if the corresponding reciprocal-lattice point never touches the Ewald sphere. According to the model B, we can calculate an average tilt angle of the undulated layer. The values are in a good agreement with the observed ones as listed in Table 1.

Analysis of crystal structure gives us more information about molecular conformation and packing in the elongated fibers. On the crystallization, the elongated fibers were fixed with their length and annealed at 140 °C below T_m. Figure 7a−d shows the crystal patterns of original fiber and elongated fibers with the strains of 5, 10, and 15%.

Table 1. Tilt Angles of the Smectic Layer Observed in the Elongated Fibers

elongation ratio/%	tilt angles/deg	
	observed[a]	calculated[b]
5	20 (20[c])	17.8
10	25 (26[c])	24.6
15	28 (29[c])	29.6

[a] Estimated from the azimuthal intensity profile of the second layer reflections. [b] Calculated by the assumption that the stretched conformation is altered to the initial zigzag one without changing the fiber dimension (see the text). [c] Estimated from the splitting angles of (004) reflection in the crystal fibers.

We first refer to the crystal structure of the original fiber. The reflections can be indexed by the monoclinic lattice with $a = 5.84$ Å, $b = 5.10$ Å, $c = 30.3$ Å (chain axis), and $\gamma = 56.0°$ as listed in Table 2. One molecule runs through this unit and two repeating units are

Table 2. Bragg Spacings and Intensities of BB-5 Crystal

d_{obs}/Å	intensity	*hkl*	d_{calcd}/Å[a]
15.0	vs	002	15.1
7.52	vs	004	7.57
5.05	w	006	5.05
4.84	vs	100	4.84
4.64	vw	102	4.61
4.13	vs	104	4.08
3.84	s	105	3.78
3.52	vw	106	3.49
4.23	vs	010	4.24
4.18	vs	011	4.19
4.09	m	012	4.08
3.91	s	013	3.91
3.71	m	014	3.70
3.48	s	015	3.47

[a] Based on the monoclinic lattice with $a = 5.84$ Å, $b = 5.10$ Å, and $c = 30.3$ Å; $\gamma = 56.0°$ (see text).

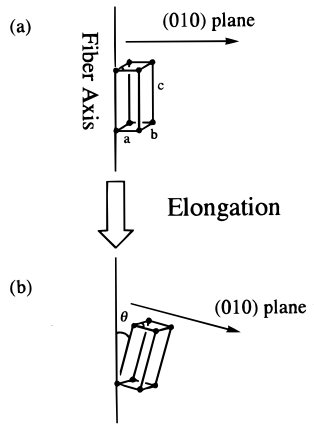

Figure 8. Unit cell in (a) the original BB-5 fiber and (b) the elongated one depicted from the variation in the X-ray patterns under elongation shown in Figure 7. The tilt direction of the unit cell coincides with *c*-director of the SmCA structure. The fiber axis is in a vertical direction.

included along *c*-axis. We have not determined the atomic positions but can suggest a similar zigzag arrangement of mesogenic cores as in the SmCA phase since the length of repeating unit (15.1 Å) along the chain axis is similar to that (15.4 Å) of the SmCA phase, and the reflections are relatively strong in an azimuthal direction around 25° from the equator.[12]

The elongated fibers show the reflections with the same spacings as the original fiber, although the diffraction geometry of the reflections is remarkably altered (compare Figure 7b−d with Figure 7a). This means that the basic crystal lattice is the same for all the elongated fibers but that the molecular chain axis (*c*-axis) is tilted with respect to the fiber axis as considered above. To clarify this point, the unit cell was tilted with several angles and resulting diffraction pattern was examined. Here, the tilt angle, θ, was determined from the splitting angle of (004) reflections. As listed in Table 1, the tilt angles correspond to those observed in the SmCA glassy fibers. On the other hand, the reflections on the (01*l*) line in Figure 7 do not shift so much by the elongation (compare Figure 7a with Figure 7b−d). Especially, the (010) reflection is not affected at all. In contrast, the reflections on the (10*l*) line shift significantly. These simply indicate that the tilting arises along the (010) planes. As a reason for this particularly preferred direction of tilt, this direction may agree with a *c*-director (or tilt direction) of the mesogenic groups in the SmCA phase. Figure 8 illustrates the tilting of unit cell in a real space. The diffraction

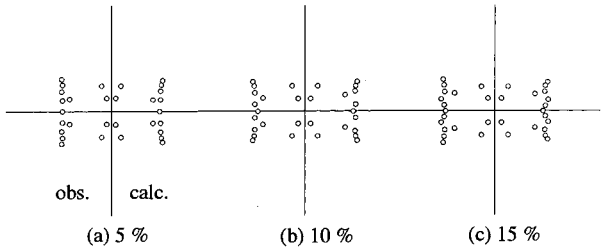

Figure 9. Comparison of the observed reflections (left) and the predicted reflections (right) for the crystalline BB-5 fibers elongated with a strain of (a) 5%, (b) 10%, and (c) 15%. The reflections are calculated from the tilting of crystal lattice as illustrated in Figure 8. The fiber axis is in a vertical direction.

patterns derived from the tilting of unit cell can be obtained by using the equation reported by Bunn et al.[14] They are compared with the observed ones in Figure 9. All the predicted reflections given in a right-hand side section of the figure showed a good agreement with those of the actually observed patterns (left-hand side) in every elongated fiber. We thus reach the conclusion that the elongated fibers form the same crystal as the original fiber but the crystal layer is tilted. This obviously supports model B of Figure 2d as the deformed structure forced by the elongation.

Conclusion

By drawing the isotropic melt of BB-5 polyester, we obtained the highly oriented fiber of glassy SmCA phase. The elongation was applied at 20 °C just below the glass transition temperature of around 50 °C. In this glassy SmCA fiber, the mesogenic groups within a chain are arranged in a characteristic zigzag fashion, and so the fiber could be elongated until the mesogenic groups lie parallel to each other. Immediately after the elongation, however, such a stretched chain is relaxed to recover the initial zigzag conformation, resulting in the characteristic undulation of the smectic layers. Thus, the elongation deformation until 15%−20% is conserved on unloading. On heating this deformed fiber to the SmCA temperature, the undulation disappears and the initial orientation completely recovers.

More recently, the elongation deformation has been examined for the network polymer systems forming smectic liquid crystals.[15−17] All these studies, however, have been performed for the polydomain elastomer. The present results collected for the uniaxially oriented fiber are helpful to understand the structure change induced by the elongation of the smectic elastomer.

References and Notes

(1) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278; **1989**, *22*, 4083.
(2) Watanabe, J.; Kinoshita, S. *J. Phys. II* **1992**, *2*, 1273.
(3) Tokita, M.; Osada, K.; Watanabe, J. *Liq. Cryst.* **1998**, *24*, 477.
(4) Watanabe, J.; Hayashi, M.; Kinoshita, S.; Niori, T. *Polym. J.* **1992**, *24*, 597.
(5) Watanabe, J.; Nakata, Y.; Shimizu, K. *J. Phys. II* **1994**, *4*, 581.
(6) Watanabe, J.; Hayashi, M.; Morita, A.; Tokita, M. *Macromolecules* **1995**, *28*, 8073.
(7) Watanabe, J.; Hayashi, M.; Tokita, M. *React. Funct. Polym.* **1996**, *30*, 191.
(8) Tokita, M.; Takahashi, T.; Hayashi, M.; Watanabe, J. *Macromolecules* **1996**, *29*, 1345.
(9) Watanabe, J.; Tokita, M.; Osada, K.; Kawauchi, S. *Polym. J.* **1998**, *30*, 589.
(10) Watanabe, J.; Hayashi, M.; Nakata, Y.; Niori, T.; Tokita, M. *Prog. Polym. Sci.* **1997**, *22*, 1053.

(11) Tokita, M.; Osada, K.; Watanabe, J. *Polym. J.* **1998**, *30*, 687.
(12) Kaneko, T. I.; Imamura, K.; Watanabe, J. *Macromolecules* **1997**, *30*, 4244.
(13) Clark, N. A.; Meyer, R. B. *Appl. Phys. Lett.* **1973**, *22*, 493.
(14) Daubeny, R. de P.; Bunn, C. W.; Brown, C. J. *Proc. R. Soc. London* **1954**, *A226*, 531.
(15) Nishikawa, E.; Finkelmann, H. *Macromol. Chem. Phys.* **1997**, *198*, 2531.
(16) Ortiz, C.; Wagner, M.; Bhargava, N.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1998**, *31*, 8531.
(17) Ortiz, C.; Ober, C. K.; Kramer, E. J. *Polymer* **1998**, *39*, 3713.

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