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Unusual Formation of Smectic A Structure in Cross-Linked Monodomain Elastomer of Main-Chain LC Polyester with 3-Methylpentane Spacer

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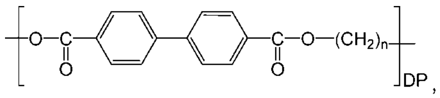
ABSTRACT: The main-chain BB/PDA-5(3-Me) polyester containing a photo-cross-linkable *p*-phenylenediacrylate (PDA) moiety was synthesized and cross-linked in the transparent monodomain smectic CA (S_{CA}) state by UV irradiation. The monodomain S_{CA} elastomer contracted to about 60% of the original length on heating up to the isotropic phase and recovered only 5% of the original length at the liquid crystallization on cooling. Irrespective of such a small recovery in the length, the liquid crystal was well formed with a high orientation, but the formed smectic structure was of a smectic A (S_A) type with the layer spacing 2 times larger than that of the original S_{CA} phase. By elongation of this contracted elastomer, the S_A structure transformed to the original S_{CA} one, showing a quasi-plateau in the stress–strain curve. The connection between the structural transformation and the stress–strain behavior lets us propose an unsusal S_A structure in which the polymer chain folds every two repeat units. Such a characteristic folding structure may be caused by the limited mobility of the mesogens in the network.

1. Introduction

Main-chain liquid crystalline (LC) polymers have mesogenic groups linked to each other by a flexible spacer. Because the mesogens within a backbone form the mesophase structure, the polymer chain itself must adopt a conformation compatible with the structure of mesophase. Such a conformational constraint has been clarified through the studies on the smectic phases formed by the following main-chain LC polymers:[1−11]



which are designated as BB-*n* where *n* is the number of carbon atoms in the spacer. Most significant coupling of polymeric and mesogenic properties reflects on the type of smectic phase which appears different between the odd- and even-membered BB-*n*; BB-*n* with even *n* forms an ordinal smectic A (S_A) phase, while that with odd *n* forms a distinct smectic CA (S_{CA}) phase in which the mesogens tilt with respect to the layer normal with their tilt direction opposite between the neighboring layers.[2,3,7] The layer spacings as well as the formation of such two types of smectic structure have been well explained by assuming that the more extended polymer chain penetrates many layers.[10]

Because of this direct coupling of the liquid crystalline order with the polymer conformation, more recently, the main-chain type of LC elastomer has attracted great attention.[12−21] If the highly oriented LC elastomers are prepared, a large strain thermal actuation would be expected along the n-director or polymer chain direction with the temperature variation in the LC temperature region and further at the LC-to-isotropic transition, leading to the unique mechanical properties and potential applications as mechanical actuators.[15] The LC elastomers also present challenging problems for fundamental science, soft elasticity related to LC structures, shape memory and pattern formation on liquid crystallization, unusual formation of LC structures, and so on.[12]

In this paper, we report the anomalous formation of a S_A phase in a photo-cross-linked BB/PDA-5(3-Me) elastomer in which photo-cross-linkable *p*-phenylenediacrylate (PDA) units are incorporated into the BB-5(3-Me) polyester (refer to Figure 1). In the preparation of elastomer, at first, the transparent monodomain S_{CA} phase of un-cross-linked BB/PDA-5(3-Me) was prepared by stretching the isotropic melt, and then photo-cross-linked by UV irradiation. The S_{CA} structure was not damaged by the cross-linking, but once the elastomer was heated up to the isotropic melt, it did not recover the S_{CA} phase but formed a S_A phase with the layer thickness 2 times larger than the repeating unit length. Such a peculiar formation of the S_A phase in the elastomer is discussed in relation to the folding of polymer chains which is forced due to limited molecular mobility in the network.

2. Experimental Section

2.1. Materials. The BB/PDA-5(3-Me) polyester was synthesized by melt transesterification of dimethyl *p*,*p*′-bibenzoate (13.3 mmol), dimethyl *p*-phenylenediacrylate (1.84 mmol), and 3-methyl-1,5-pentanediol (31.3 mmol) with isopropyl titanate as a catalyst (see Figure 1). The polymer was purified by precipitation from the chloroform solution to methanol and dried in vacuo. Molecular weight and molecular weight distribution were determined as M_n = 37 700 and M_w/M_n = 2.3, respectively, from the GPC curve which was calibrated with a polystyrene standard. The molar fraction of the *p*-phenylenediacrylate (PDA-5(3-Me)) unit in the copolymer (ϕ_{PDA}) was determined by an integration of each signal in the ^{1}H NMR spectrum for aromatic protons in BB at $\delta = 7.52$ or 8.03 and *trans* alkene protons and aromatic protons in PDA at $\delta = 6.39$ and 7.45, respectively. ϕ_{PDA} thus determined is 0.12, corresponding to that in feed, indicating that the double bond of the cinnamoyl group in PDA sustains perfectly after high temperature polymerization. BB/PDA-5(3-Me) forms the well-known S_{CA} phase the same as BB-5(3-Me).[8,9] It shows glass transition at T_g = 29 °C and S_{CA}−isotropic transition at T_i = 140 °C with an enthalpy change (ΔH_i) of 3.3 kJ mol^{-1} on heating, as found in the differential scanning calorimetry (DSC) curve in part a of Figure 2. These data are comparable to those for BB-5(3-Me): T_g = 30 °C, T_i = 150 °C, ΔH_i = 3.8 kJ mol^{-1}.

2.2. Methods. DSC measurement was carried out with a Perkin-Elmer Pylis 1 DSC calorimeter at a scanning rate of 10 °C min^{-1}

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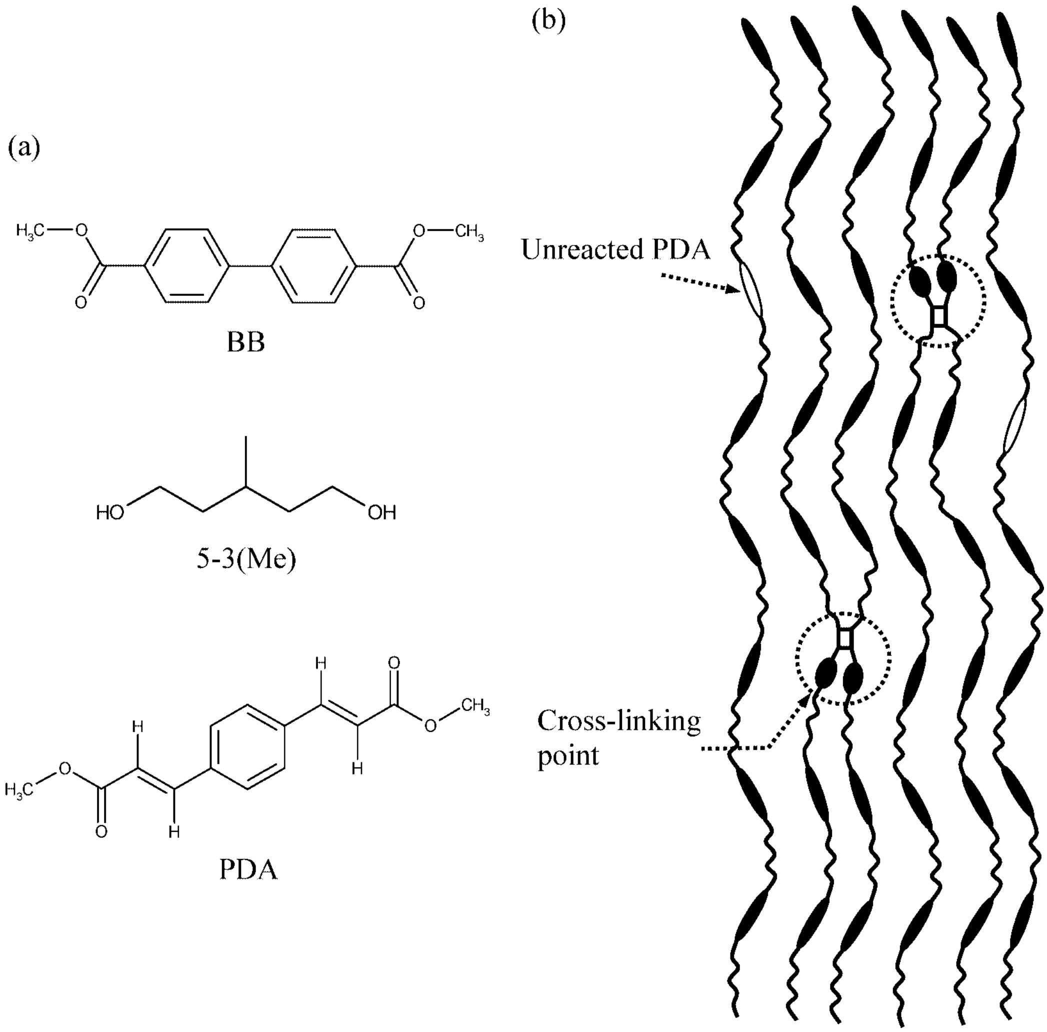

Figure 1. (a) Chemical structures of reactants for polymerization and (b) schematic illustration of smectic elastomer of the main-chain BB/PDA-5(3-Me) polyester.

under a flow of dry nitrogen. Wide-angle X-ray diffraction (WAXD) was recorded on an image plate using a Rigaku RINT-2000 with monochroic Cu Kα radiation from single graphite crystal of monochromator. ^{1}H NMR and FT-IR spectra were measured by JEOL JNM-AL400 and JASCO MFT-2000, respectively.

The temperature dependence of strain for the elastomer was obtained by a Seiko Instruments TMA/SS 150C. The elastomer in film form with a thickness of 0.1 mm was cut into rectangular strips with 10 mm length (in the polymer chain direction) and 2 mm width, and clamped in the tensile testing machine. The sample was heated and cooled at a rate of 2 °C min^{-1} under dry nitrogen atmosphere and the sample length (L) was measured. The strain was defined as $\{(L - L_0)/L_0\} \times 100\%$, where L_0 is the length of the original sample. The stress–strain curve was measured by a Linkam TST350 temperature control tensile stage, and the X-ray pattern of the stretched sample was measured simultaneously by mounting the tensile stage on the X-ray diffractometer.

3. Results and Discussion

3.1. Preparation of Monodomain Smectic Elastomer by Photo-Cross-Linking. At first, the monodomain S_{CA} film of BB/PDA-5(3-Me) with a thickness of about 100 μm was prepared by drawing the isotropic melt at 160 °C at a rate of 20 cm s^{-1} by tweezers. After the film was annealed at 70 °C for 12 h to ensure perfect liquid crystal formation, the film became completely transparent, and then photo-cross-linked by UV light irradiation (λ_{max} = 365 nm, 9 mW cm^{-2}). The cross-linking reaction was monitored by measuring the FT-IR spectra of the UV irradiated film,[22,23] as shown in Figure 3. Before irradiation, the stretching mode of C═C bonds in the PDA unit appeared at 1635 cm^{-1}. Upon irradiation, its intensity decreased due to the formation of new unconjugated carbonyl groups to work as a cross-link.[22] Calculated from the intensity variation at 1635 cm^{-1}, 40% of C═C bonds in the PDA had reacted by UV irradiation for 200 min, and only the negligible increase in the conversion was observed for more irradiation. Thus, 5% of the repeating units of BB/PDA-5(3-Me) with ϕ_{PDA} = 0.12 participate in cross-linking. This value corresponds to the theoretically calculated one of 4.3%,[24] meaning that the 20 repeat units on average are included between two successive cross-link points.

In the photo-cross-linking elastomer, a highly oriented monodomain structure was conserved, as found from the X-ray diffraction pattern in part a of Figure 4. Here, an X-ray beam was irradiated on the face of the film which was set with the drawing direction in the vertical direction. The diffraction pattern includes sharp reflections in the small-angle region on the meridian and a broad halo in the wide-angle region having intensity maxima above and below the meridian. This feature is characteristic to the S_{CA} phase in which the mesogens tilt with respect to the layer normal and the tilt direction alternates between the neighboring layers.[2,3,7] The smectic layer spacing

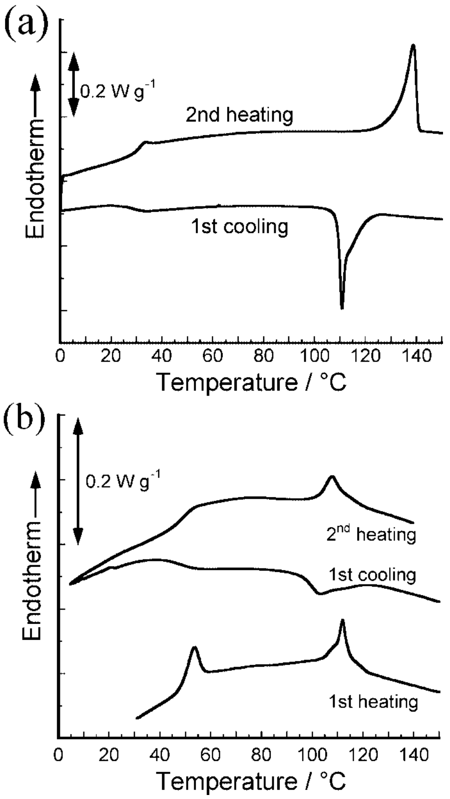

Figure 2. DSC thermograms of BB/PDA-5(3-Me) polyester measured for the samples on (a) first cooling and second heating processes with bulk sample before UV irradiation and (b) first cooling and first and second heating processes with the UV photo-cross-linked monodomain elastomer. The heating and cooling rates were 10 °C min^{-1}.

is 16.3 Å which coincides with that of the S_{CA} phase in the un-cross-linked BB/PDA-5(3-Me) polyester. Thus, we know that the S_{CA} layer structure as well as its orientation retains completely during the photo-cross-linking reaction.

3.2. Thermal Transition of BB/PDA-5(3-Me) Elastomer and Its Shape Change along the Director at Smectic-to-Isotropic Transition. Part b of Figure 2 shows the DSC curve of BB/PDA-5(3-Me) elastomer. Here, the DSC data were collected on the first cooling run after the elastomer was heated up to the isotropic melt, and then on the second heating run. The elastomer shows $T_g = 50$ °C, $T_i = 107$ °C, and $\Delta H_i = 0.8$ kJ mol^{-1}, as found from the second heating data. In comparison with the DSC data of BB/PDA-5(3-Me), the glass transition appears at higher temperature and the isotropization takes place in a wider and lower temperature range. Further, ΔH_i is less than half of that in the un-cross-linked material, which suggests the smaller degree of liquid crystallinity and/or less ordered smectic structure in the elastomer.

It is interesting to know how the length of the sample along the director changed on the smectic-to-isotropic transition. The result is shown in Figure 5. On heating to the isotropic melt, the as-cross-linked monodomain S_{CA} film contracted to 60% of the original length (L_0) in the layer normal direction (i.e., polymer chain direction). This shape change is similar to that reported for the smectic elastomer by Beyer et al.[21] but fairly smaller than the length change of about 500% observed for nematic elastomer by Ahir et al.[20] Small shrinkage for the present smectic elastomer may be related to the smectic character of the main-chain LC polymer in which the polymers penetrate into many smectic layers but form a large size of lamella forming the chain folding.[4,6,8–11,25]

Figure 5 also shows that on cooling to the LC phase the contracted film recovered only 5% of L_0, which is extremely smaller in a comparison with the 40% length reduction on the S_{CA}-to-isotropic transformation of the original elastomer. On further heating and cooling cycles between the smectic and isotropic phases, the contraction and extension by 5% of L_0 were reversibly observed.

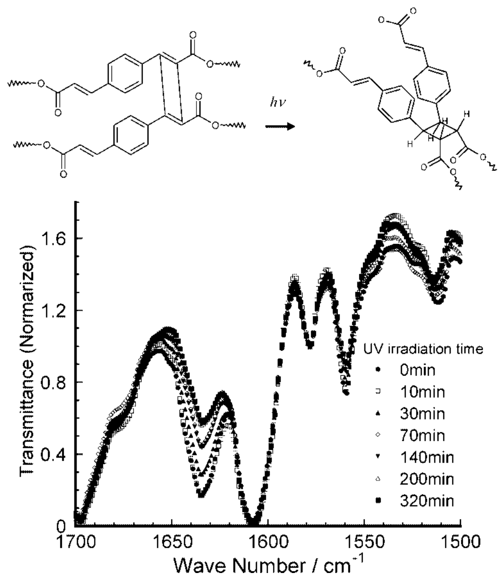

Figure 3. Infrared spectra of the thin films of BB/PDA-5(3-Me) polyester irradiated by UV for different periods indicated in the figure. The scheme of the photo-cross-linking reaction occurring in the PDA units is illustrated in the upper part.

3.3. Unusual Formation of the S_A Phase in Elastomer and Its Characteristic Folding Structure. X-ray diffraction patterns of the elastomer measured at 150 °C (Iso phase) and 80 °C (LC phase) are shown in parts b and c of Figure 4, respectively. The diffraction pattern at the isotropic temperature of 150 °C includes only a ring-shaped halo at a wide angle as expected, but the azimuthal intensity plot shown on the right side shows that the outer halo is somewhat concentrated on the equatorial line. It suggests that the molecular orientation in the original sample was not completely eliminated in the isotropic liquid state. On cooling to a smectic temperature of 80 °C, the orientation was recovered; the pattern shows sharp reflections on the meridian and broad halos concentrated on the equator. Thus, the mesogenic groups orient spontaneously on the liquid crystallization. The small but clear extension of the elastomer on the isotropic-to-smectic transition is attributable to the orientation recovery of the mesogenic groups.

Here, three distinct points are cited. First is that, irrespective of the fact that only 5% recover in length, the orientation order was sustained to the same extent as that in the original S_{CA} film (compare parts c and a in Figure 4); the determined degree of orientation of the smectic layer ($\langle P_2 \rangle$) is 0.98 for the original S_{CA} and 0.93 for the smectic phase of the contacted elastomer.[9] Second, the resulting smectic phase was a type of S_A which is exceptional for BB/PDA-5(3-Me) with odd-number carbons in the alkyl spacer backbone.[8,9] Third, the layer spacing of 32.2 Å in the S_A phase was twice as long as the layer spacing of 16.3 Å in the original S_{CA} phase, meaning that each S_A layer includes two repeat units.

Here, the question arises of how such a high orientation was achieved in the contracted film with only a 5% extension in length from the isotropic state. The answer can be given by the regular formation of chain folding structure, in which the high orientation is achieved only for mesogens but not for polymer chains. In other words, the polymer chain tends to be accommodated into a limited number of layers. This is completely

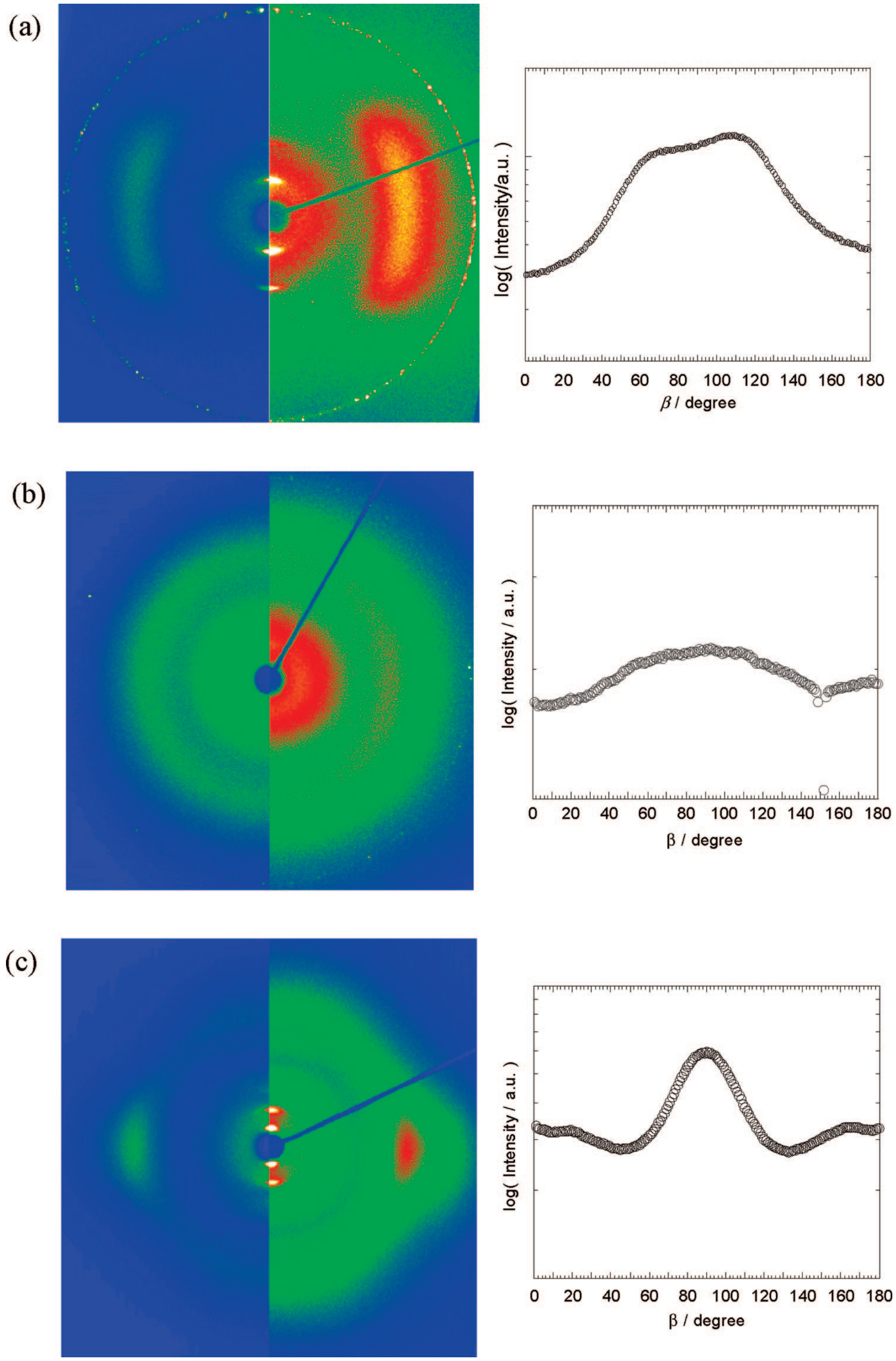

Figure 4. X-ray diffraction pattern of the photo-cross-linked BB/PDA-5(3-Me) elastomer film: (a) as-cross-linked, (b) in the isotropic phase at 135 °C, and (c) in the LC phase at 80 °C cooled from the isotropic phase. The intensity distribution measured as a function of the azimuthal angle (β) at a diffraction angle of $2\theta = 20.5°$ is shown on the right side of the pattern. The meridian direction corresponds to $\beta = 0°$.

different from that in the smectic phase of the un-cross-linking polyester in which an extended polymer chain penetrates into many layers.

From conformational analysis of the main-chain polyester, one knows that the folded chain configuration is allowed for the odd-membered polymers. Conformational analysis shows that the angle made by unit vectors attached to two mesogens connected by a five methylene spacer can distribute in the region of 150–180° in addition to that of 50–90°.[10,11,26] The latter distribution has explained the zigzag alignment of mesogens that conforms to the S_{CA} structure.[1,2,7,10,11] In the former distribution, in contrast, two successive mesogens can arrange parallel to each other by the hairpin folding. Thus, it is reliable that the chain folding at the spacer site is regularly formed to fit the S_A structure. To explain the layer spacing that is twice as long as the repeating unit length, we propose that a polymer chain folds in each of two repeating units, as illustrated in Figure 6. In this model, the spacer group in the central part might force the neighboring mesogens to tilt to each other as in the S_{CA} phase, but the 2-fold symmetry of the chain folding part may

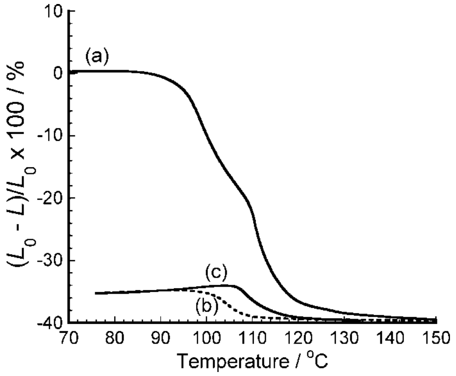

Figure 5. Change of the strain $(L_0 - L)/L_0 \times 100\%$ along the layer normal direction of the monodomain smectic elastomer on first heating (curve a) and cooling (curve b) processes, and second heating (curve c) process. L_0 is the length of the original elastomer at room temperature.

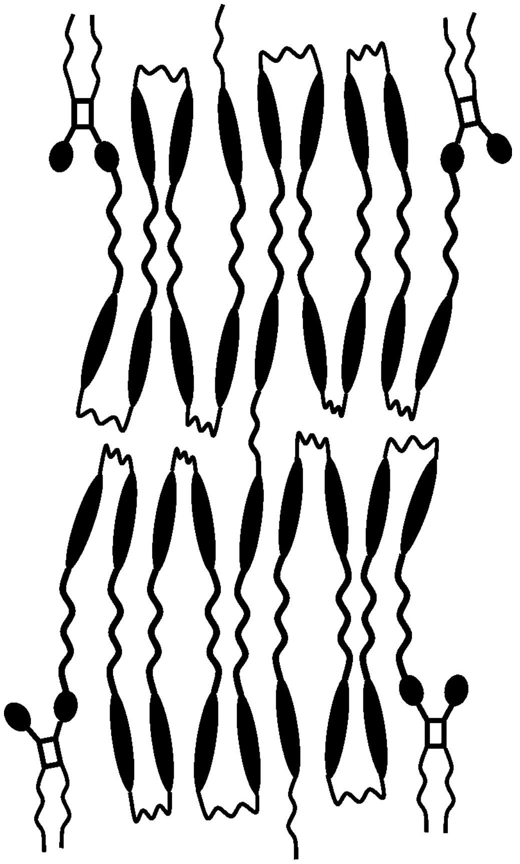

Figure 6. Illustration of the chain folding structure presumed for the contracted S_A film. Here, the folding appears in each of two repeating units.

compensate this force so that the mesogens within a layer are packed uniaxially into the S_A phase which may be energetically stable. The reason, however, is not clear on why the folding appears in each of two units but not in each unit.

Such an unusual formation of the S_A may be due to the limited mobility of the polymer chain in the network, that is, the lack of the freedom to achieve the more extended conformation which is more favored energetically.

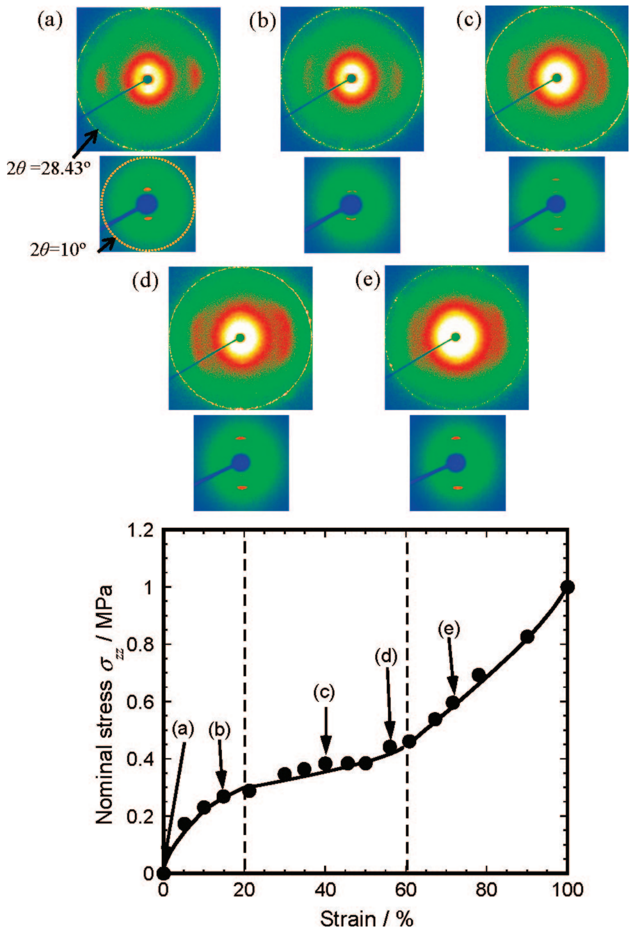

Figure 7. Stress–strain curve of the BB/PDA-5(3-Me) elastomer film cooled from the isotropic melt to the LC phase at 80 °C. The stress was measured at 40 min after the sample had been elongated at 80 °C at a strain rate of 10% $\min^{-1}$ and kept at a predetermined strain. The X-ray diffraction patterns inserted in the graph were measured for the original unstrained sample (a) and the sample elongated at a strain of 17% (b), 41% (c), 55% (d), and 75% (e). Below each WAXD pattern, the small-angle region is shown clearly with appropriate contrast and magnification. The elongation axis is in the vertical direction.

3.4. Stress–Strain Behavior of Monodomain S_A Elastomer. By applying stress to the contracted monodomain S_A elastomer in the layer normal direction, the length was recovered to the original length of the monodomain S_{CA} elastomer initially prepared. The liquid crystal structure in the elastomer during this elongation process was investigated by simultaneous measurements of stress and X-ray diffraction pattern for the elongated film at a predetermined strain. Here, the smectic film was elongated at 80 °C at a strain rate of 10% $\min^{-1}$ to a predetermined strain and kept for 40 min, during which the stress relaxed into a constant value. The elastomer can be elongated up to about 100% (corresponding to $1.2L_0$) without breaking. The remaining stress is plotted against the strain in Figure 7. The resulting stress–strain curve is divided into three regions with different slopes: on increasing strain, the stress increases steeply in strain region I of 0–10%, takes an almost constant value in region II of 10–55%, and then increases again in region III of 55–100%. The X-ray diffraction patterns measured simultaneously show changes distinctive of these three regions (see the photographs in parts a−e of Figure 7). In region I, while the outer halo does not show significant change on elongation, the first-order layer reflection at the smallest angle was spread and split into two spots at an angle of 25° to each other in the azimuthal direction, suggesting that the smectic layers were undulated. In region II, the first-order layer reflection decreased its intensity and then the second-order one became dominant. Simultaneously, the outer halo began to spread in the azimuthal direction and its intensity showed a bimodal distribution with maxima on both sides of the equatorial line (see Figure 8). Thus,

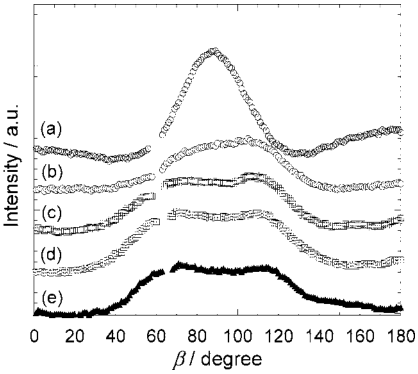

Figure 8. The intensity distribution measured as a function of the azimuthal angle (β) at a diffraction angle of $2\theta = 20.5°$ for the diffraction patterns shown in Figure 7. Curves a, b, c, d, and e are collected from parts a, b, c, d, and e of Figure 7, respectively. The meridian direction corresponds to $\beta = 0°$. The lack of data at an angle of around 65° is due to the shade of the beam stopper support.

the overall diffraction pattern became similar to that of the original S_{CA} phase (see the photograph in part e of Figure 7). In region III, the first-order reflection disappeared completely at a strain of 75% which corresponds to the original length (L_0). The S_A structure was thus altered to the ordinal S_{CA} one on the elongation to the original length. The quasi-plateau (region II) in the stress–strain curve can be well explained by unfolding of chains.[9,27,28] The S_A-S_{CA} structural transformation thus took place simultaneously with the unfolding of the chains; in other words, in the foregoing S_A phase, the polymer chain should be folded.

4. Conclusion

In conclusion, we synthesized the photo-cross-linkable main-chain smectic LC BB/PDA-5(3-Me) polyester having the PDA unit as a photoreacted moiety and succeeded in preparing the monodomain S_{CA} elsatomer by UV irradiation on the thin transparent film drawn from the isotropic melt. The monodomain elastomer contracted to 60% of the original length on heating up to the isotropic phase and recovered 5% in length at the liquid crystallization on cooling. In the contracted film, a S_A structure was newly formed with a layer spacing twice as long as the repeating unit length and with a high degree of orientational order the same as the original S_{CA} one. By elongation, the S_A structure is altered to the original S_{CA} one, followed by a quasi-plateau in the stress–strain curve. The connection between the phase transformation and the stress–strain behavior leads to the conclusion that the unusual formation of the S_A phase in the elastomer can be caused by the chain folding due to the limited mobility of the polymer chain in the network. Overall results show that the chain folding preferentially arises in each of two repeat units to form the S_A structure.

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