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Temperature gradient-cooled smectic A phase orientation and its effects on C1 orientation in ferroelectric liquid crystals

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The temperature gradient cooling of ferroelectric liquid crystals (FLCs) confined to a closed long narrow rectilinear space causes the molecules constituting the smectic layers to acquire significant movement. The ordinary layer structure of the SmA phase consequently undergoes deformation which in turn determines the mode of the SmA → SmC* phase transition. SmA stripe-shaped texture was found to result from molecular movement only when the direction of the temperature gradient is the same as the rubbing direction. For FLCs whose SmA temperature range exceeds 20°C, the SmA phase undergoes virtually defect-free C1 orientation without change to C2 orientation, when the direction of the temperature gradient is opposite that of rubbing. Defect-free C2 orientation is possible irrespective of the SmA temperature range in temperature gradient cooling. C1 and C2 orientations may combine with no zigzag defects through the use of such FLCs.

1. Introduction

The zigzag-free smectic layer structure is an essential element in display devices incorporating ferroelectric liquid crystals (FLCs) [1, 2] or antiferroelectric liquid crystals [3, 4]. The layer structure is situated between a pair of glass plates separated by an interval of 2–1·4 μm. This system usually assumes the chevron layer structure in which the layers bend about 10–20° at the middle of the cell gap [5], as shown in figure 1. Two opposite bend directions parallel to the layer normal direction are possible. Zigzag defects constitute the boundary of two macroscopic domains whose bend directions are opposite [6]. Rubbed thin polyimide film determines the normal direction and molecular orientation, as twisting or uniform in each layer [7] but never precisely the bend direction over whole layers. For example, zigzag-free orientation would not be possible in a cell with antiparallel rubbing because of equal probability of the formation of two domains opposite in bend direction [8].

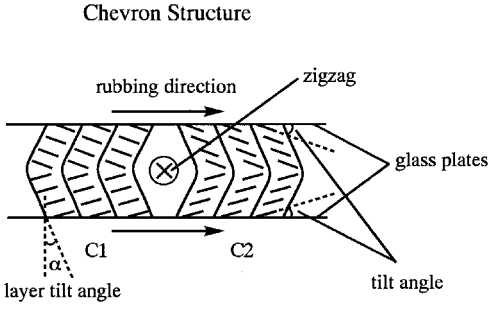

Figure 1. C1 and C2 orientation in the chevron layer structure.

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Phase changes from SmA to SmC* are complex, depending on the direction of rubbing of a pair of polyimide films. For antiparallel rubbing, two domains opposite in bend direction grow from the SmA phase at the same time, giving rise to zigzag defects; structural change occurs in a single step. In the case of parallel rubbing, all smectic layers first bend in one and the same direction (≪) which subsequently is reversed and structural change occurs in two steps (≪ → ≫). This reversal may not proceed to completion over whole layers. The orientation of the domain which grows first from SmA is C1 and that from C1, is C2 [9]. The layer bend direction of either orientation may be the same or opposite to that of rubbing, as shown in figure 1. C2 orientation is usually attended by line-like defects, indicating its derivation from C1 orientation [8]. Application of an a.c. field at 100–300 Hz may serve to eliminate line-like defects in some cases, but this method is impracticable [10].

In the case of antiparallel rubbing, zigzag defects can be eliminated by having the layer bend direction fixed arbitrarily in one of the two possible directions. With parallel rubbing, zigzag and line-like defects can be eliminated with only a one-step structural change such as SmA → C1 or SmA → C2 [8]. In these cases, liquid crystal molecules must move in one direction normal to

the smectic layer. If there is sufficient molecular movement in the SmA phase, self-alignment with orientation better than that initially possible will occur, or layer deformation similar to that of a chevron structure will come about owing to elasticity of the layers.

The cell structure and cooling method that bring about molecular movement were presented in detail in a previous paper [8]. In that study, liquid crystal molecules were confined to a long narrow rectilinear space, 300 μm in width and cooled from one end to the other. A suitable temperature gradient was applied parallel to the layer normal direction, essentially the same as that of rubbing. Rubbing was carried out parallel to the length of the rectilinear space. The confined molecules moved continuously toward the low temperature side due to volume contraction.

In the case of antiparallel rubbing, completely zigzag-free orientation was attained. With parallel rubbing, defect-free C2 orientation was possible but not zigzag-free C1 orientation. This shows that temperature gradient cooling brings about layer deformation through the concerted movement of constituent molecules. Whether defect-free C1 orientation is possible is a purely technical matter. To determine whether layer deformation actually occurs is of fundamental concern and was the purpose of this study by temperature gradient cooling in the SmA phase. Layer deformation may possibly be required for the achievement of C1 orientation free from zigzag defects.

In FLCs it is very difficult, if not impossible, to prevent the structural change of C1 → C2. However, defect-free C1 orientation should lead to greater display device quality owing to its stable bistability and high degree of contrast. Kanbe *et al.* consider the polyimide/FLC system with high pre-tilt angle ideal for achieving such orientation [9]. But the incorporation of this system into a cell is difficult and the viewing angle becomes somewhat narrow. C1 and C2 orientation cannot be combined without defects since a high pre-tilt angle does not permit C2 orientation. Proper use of the temperature range of the SmA phase may help solve this problem. The broader the temperature range of the SmA phase, the greater is the extent of SmA layer deformation. Deformation is a major determinant of structural change at the time of the phase change SmA → SmC*. An attempt was thus made to achieve zigzag-free C1 orientation using FLCs with an SmA temperature range exceeding 20°C, and a study was made to determine whether C1 and C2 domains can exist without zigzag defects.

2. Experimental

Liquid crystal molecules must be confined in a rectilinear space completely closed off except for the inlet and outlet sites of their introduction. Two glass plates accommodating many rectilinear spaces were connected to each other by numerous barriers running parallel to each other and made of positive or negative type photo-resist. These barriers were attached to the glass plates by conventional photolithography.

Polyimide solution HL1110 (Hitachi Kasei Kogyo) or SE610 (Nissan Kagaku Kogyo) was spin-coated onto a thoroughly washed A4 size glass plate and dried at 180°C to obtain a thin polyimide layer of the proper thickness. Photo-resist solution (MP1400, positive type, Shipley, or negative type resist specially designed at this laboratory) was spin-coated over the polyimide layer and pre-baked at 90°C. The photo-resist was exposed to UV light through a striped mask and developed with an alkaline developer such as MF312 (Shipley). It was necessary to dissolve the photo-resist so that none remained on the polyimide layer; it was also necessary to avoid damage to the polyimide layer by the developer. Neither of these agents were allowed to have any effect on the polyimide layer. Post-baking was carried out at 140–150°C for 1 h and the stripe barriers became attached to the polyimide layer. The polyimide layer was rubbed several times in one direction parallel to the barriers, taking care not to damage them. Standard barrier height, width, pitch and length were set at 1·8 μm, 30 μm, 330 μm and 18 cm, respectively.

The glass plates were placed on the barriers so as to face each other, subsequent to correction for alignment; the removal of air permitted the barriers to come into close contact with the corresponding polyimide layer. The cell was then placed in an air oven at 150°C for 1 h, followed by gradual cooling. The plates were found to adhere completely to the stripe barriers and the single space between the glass plates was partitioned into many long narrow tunnels. A tunnel cross section, flat quadrilateral in shape, was 300 μm in width and 1·6 μm in height. The cell gap was maintained within an accuracy of ±0·07 μm and there was no spreading-out of spacer beads (which would cause defects), as observed for conventional cell structure. A photo-resist which allowed for sufficient adhesion without damage to the polyimide layer was used. Cells with different tunnel lengths or widths were prepared as necessary.

The liquid crystals listed in the table were introduced into the cells and the cell aperture and edges were made water tight with epoxy resin. The cell was immersed in hot water or an air bath at a temperature controlled within an accuracy of ±0·1°C and usually set 5°C above the isotropic–chiral nematic transition temperature. It was then removed parallel to the tunnel from the air bath into ambient air at a rate of 5 mm min^{-1}. The use of the water bath ensured that a more stable temperature gradient could be applied to FLCs with a clearing point below 90°C. A temperature gradient of 2–3°C mm^{-1} was

Table. Phase transition temperatures (°C) of liquid crystals used.

Type	Compound	Phase							Temp. range of SmA/°C
		SmC*		SmA		N*		Iso.	
FLC	CS1027[a]	•	62	•	86	•	96	•	24
	CS1031[a]	•	60	•	85	•	97	•	25
	SCE8[b]	•	59	•	79	•	100	•	20
	SCE9[b]	•	61	•	91	•	115	•	30
	TM-C108[a]	•	22	•	76		—		54
LC	8CB(K24)[c]			•	33	•	41	•	

[a] Chisso Corp.
[b] Merck Ltd, UK.
[c] E. Merck, Germany.

made possible in this simple manner and was measured by a temperature sensor. The direction of the temperature gradient could be easily changed by turning the cell upside-down longitudinally, thus making possible direct comparison of two orientations in the one cell.

FLCs with the SmC* phase at room temperature show the SmA phase above 50°C. The observation of orientation by microscopy under a temperature gradient is thus difficult since 50°C is high and the cell is large. For the same reasons, X-ray scattering measurements [5] for determining layer bend angle could not be done. The achiral smectic liquid crystals 8CB from Merck and chiral TM-C108 from Chisso, both having the SmA phase at room temperature, were therefore used to determine whether the temperature gradient direction would have an effect on the structure of the SmA phase. The SmA phases of both liquid crystals take on a bookshelf structure in a 2 μm thick cell. 8CB takes on a chevron structure in a thick cell [11]. TM-C108 shows a change from bookshelf to chevron structure with the application of a d.c. electric field [12].

For 8CB or TM-C108, parallel, antiparallel and one-sided rubbing were carried out in combination on the top and bottom glass plates. Parallel rubbing was used in the case of FLCs. A cell whose two areas of opposite rubbing direction bordered on each other (multi-domain rubbing) was prepared, as shown in figure 2 (*a*). Rubbing was carried out on alternate halves of the polyimide film (the other halves being shielded with paper) using specially prepared negative type photo-resist. The orientation of the boundary between the two areas was examined.

3. Results

For both parallel and one-sided rubbing, the SmA orientation of achiral 8CB differed according to the direction of the temperature gradient. A stripe-shaped texture was observed when the direction of the temperature gradient was the same as that of rubbing [13–16].

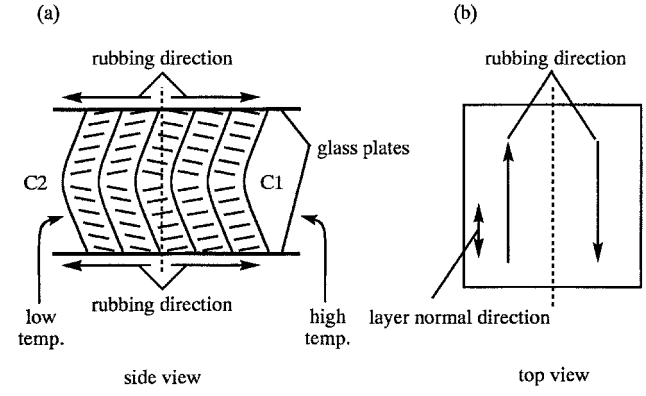

Figure 2. Two multi-domain rubbing modes for joining C1 and C2 orientations: (*a*) head-to-head, side view of cell and combined C1 and C2 orientations; (*b*) Side-by-side, top view of cell.

When the directions were opposite, no stripes were detected and the texture appeared smooth and soft, as shown in figure 3. Stripe direction was essentially parallel to that of rubbing. Stripes were fewer for narrow tunnels, as shown in figure 3 (*c*). With uniform cooling in the air bath, both orientations were observed at the same time. For one-sided rubbing, the stripes were noted to disappear very gradually; this does not occur with parallel rubbing. In antiparallel rubbing, stripes appeared regardless of the direction of the temperature gradient. For TM-C108 chiral SmA liquid crystals, no clear stripes were detected, irrespective of the direction of the temperature gradient for 300 μm or 150 μm tunnel widths.

As observed by Shao *et al.* [15], the ends of the stripe lines were sword-like in appearance and when the cell was turned under a polarizing microscope, the brightness or darkness of two neighbouring stripes was reversed. The rotation angle, ω, required for this was only 4–5°. During rotation, two parallel semi-bright lines became separated by a dark space, indicating the stripe to have taken on a paired structure. Stripe width was 1–2 μm,

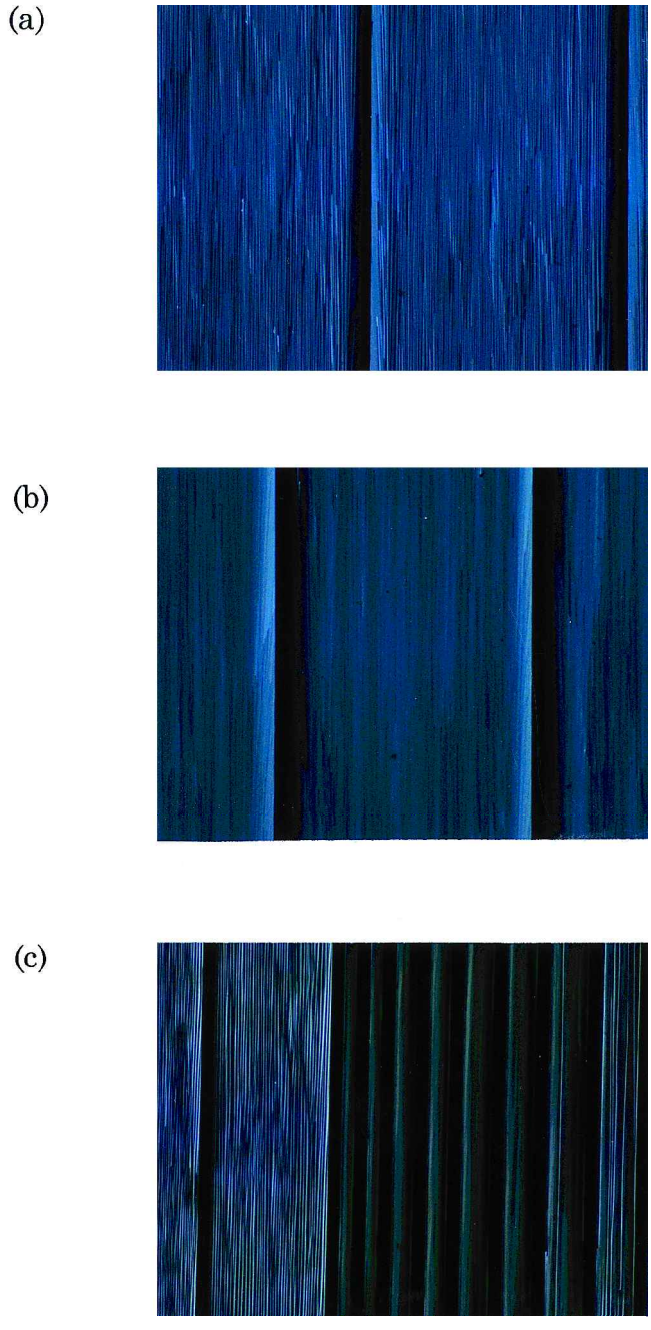

Figure 3. Stripe-shaped textures in SCB with parallel rubbing: (*a*) temperature gradient the same as rubbing direction; (*b*) temperature gradient opposite to rubbing direction; (*c*) stripe occurrence as determined by tunnel width. In (*a*) and (*b*), two broad straight lines in black barriers and tunnel width 250 μm. In (*c*), broadest tunnel width 250 μm.

basically the same as the cell gap, as pointed out by Shao *et al.* For a 4 μm cell, the stripe pitch became greater.

Zigzag defects were previously noted to decrease markedly when the SmA temperature range was greater than 20°C, with consequently almost completely defect-free C1 orientation of SCE8 or SCE9 [8]. CS1027 and CS1031 from Chisso were therefore also used to see if the same results as for SCE8 or SCE9 would be obtained. Layer bend direction was determined from the shape of a cone- or tear-like zigzag defect or from a comparison of orientations with those within or outside of the cone-like defect. Pin-holes or dust particles were often found at the sites of cone-like zigzags, as evident from figure 4 (*b*). These defects, however, do not invalidate the present method. Figures 4 (*a*), 4 (*b*) and 4 (*c*) show the typical C1 orientation of SCE9 and a comparison with C2 orientation and also what appear to be streaked abrasions (scratches) characteristic of C1 orientation. For CS1031, zigzag defects were present in tunnels 300 μm in width, but were far fewer in those half this width and absent from CS1027 and SCE9 in tunnels 300 μm wide. SCE8 showed only a few zigzag defects for the polyimide resin HL1110 in 300 μm wide tunnels, but none for polyimide SE610. Whether completely zigzag-free C1 orientation is possible could not be confirmed due to the presence of cone-like defects but the zigzags were clearly far fewer compared with those seen in the narrow temperature range of the SmA phase.

Completely defect-free C2 orientation was possible with FLCs; zigzag-free C1 orientation combined with C2 using multi-domain rubbing may thus lead to significant results. This combination was achieved by head-to-head joining in the layer normal direction or side-by-side joining in the layer direction, as shown in figures 2 (*a*) and 2 (*b*), respectively. Figure 5 shows the result of this combination using the former method for SCE8, with the two orientations being separated by a transient region 500 μm in width. Rubbing overlaps and alignment mismatches between the top and bottom glass plates resulted in the formation of a relatively wide transient region but no extremely abnormal orientation or zigzag defects were observed.

4. Discussion

The unique structural change of C1 → C2, the causes for which remain to be fully determined, gives rise to zigzag defects in the SmC* phase. Figure 6 may provide some explanation. The SmA phase takes on a layer bend structure similar to that of C1 above or at the SmA → C1 transition temperature with no zigzag defects. With decrease in temperature, layer elongation occurs in the cell gap direction as a result of compensation for the decrease in layer spacing subsequent to molecular tilting; layer bend in the C1 direction consequently becomes greater since the cell gap remains unchanged. There is a limit to layer bend. When layer bend exceeds a certain point C2 orientation occurs, requiring no large molecular displacement of $d \cos \alpha$, as schematically shown by the solid or dotted lines in figure 6 (*c*). (Here, d and α represent the cell gap and layer tilt angle, respectively.)

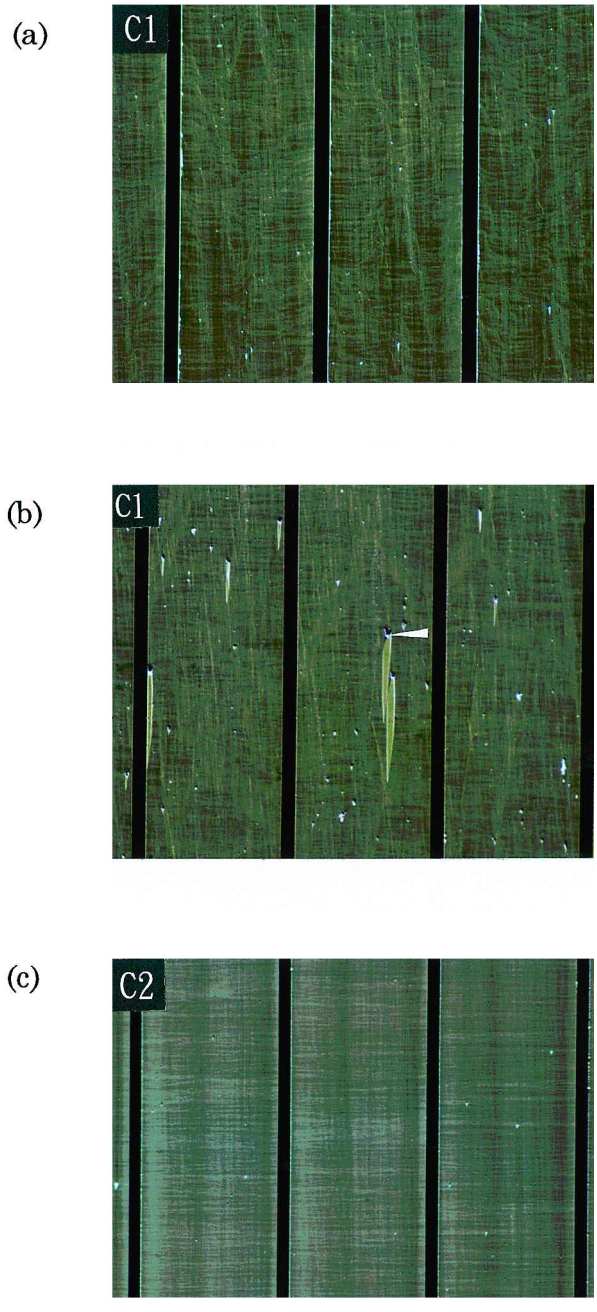

Figure 4. Comparison of C1 and C2 orientations in SCE9: (*a*) C1 orientation; (*b*) C1 orientation with cone-shaped defect; (*c*) C2 orientation. What appears to be streaked abrasions are present as characteristics of C1; C2 appears soft and smooth. Pin-holes are present at oval cone-like defects, which may disrupt the smooth movement of molecules; defect interior is the same as that of (*c*). The cell gap is about 1·8 μm; the orientation may be twisting since the texture is coloured.

C2 orientation may be more capable of absorbing layer elongation than C1, possibly since molecules in this orientation can move easily in a direction parallel to the molecular long axis.

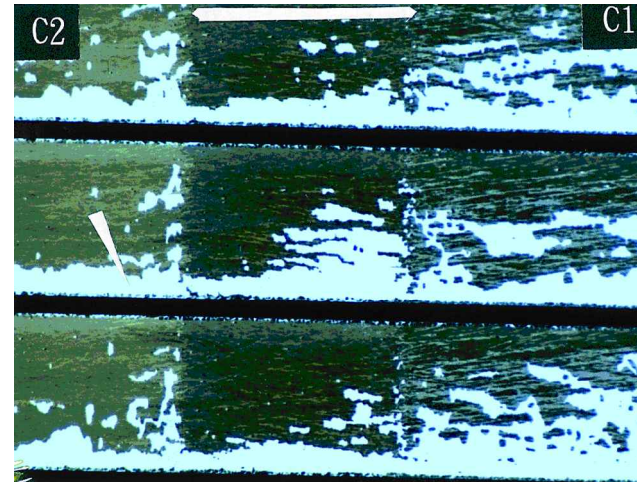

Figure 5. Combined C1 and C2 orientations: l.h.s is C2 orientation, r.h.s is C1 orientation, and the central part is a transition zone due to alignment or rubbing mismatch. Whether the central thick white areas are normal in orientation or have normal electro-optical responses is not clear. Resist layer remains on the polyimide film.

The structural change of C1 → C2 actually occurs at an early stage of layer bending in the C1 direction, 2–3°C below the SmA → C1 transition temperature, and thus starts at a specific temperature, T_{ac}, when C1 orientation assumes a definite bend. Thus, if the degree of bend in C1 differs from that at T_{ac}, C1 will never change to C2 orientation. This situation is quite likely for FLCs with a broader temperature range of the SmA phase.

In 8CB, SmA texture representing the smectic layer structure differs according to the direction of the temperature gradient. The SmA layer structure is thus clearly affected by molecular movement. In the case of FLCs, layer deformation occurs, the extent of which may be considerable for a broad SmA temperature range. Zigzag defect frequency is determined by this parameter as well as by tunnel width. For FLCs with a SmA temperature range greater than 20°C, there should be only a few or no zigzag defects for the standard temperature gradient of 2–3°C mm^{-1}. C1 orientation brought about in this manner may be unusual but electro-optical response in such a case has been shown to be normal. The polyimide/FLC system with a rather large pre-tilt angle may serve to help bring about defect-free C1 orientation [9]. The difference in zigzag frequency noted in this study when using polyimide solutions HL1110 and SE610 for SCE8 may possibly have been due to this, but this would be difficult to confirm. In contrast to C2 orientation, C1 orientation is affected by pin-holes or particles so easily that small oval cone-like zigzag defects are produced. For defect-free C1 orientation, the smooth movement of liquid crystal molecules must be maintained.

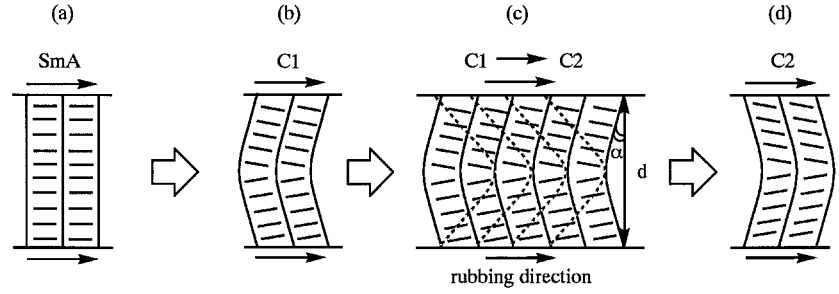

Figure 6. Structural change schematically: (*a*) SmA; (*b*) C1; (*c*) C1 → C2; (*d*) C2. SmA layers bend toward the low temperature side. The C1 → C2 structural change in (*c*) is accompanied by a small molecular displacement; d = cell gap, α = layer tilt angle.

With antiparallel rubbing, induced unidirectional layer bending completely suppresses the simultaneous formation of two domains whose bend directions are opposite; consequently, orientation free from zigzag defects comes about. With parallel rubbing, if molecules move in the direction of rubbing, SmA will move directly to C2 with no transition through C1, as pointed out previously [8].

The present method makes it possible to combine C1 with C2 orientations without zigzag defects. This combination may easily lead to grey levels at each pixel in a matrix-driven display device if the threshold properties of C1 and C2 orientations differ. Orientation as shown in figure 5, may then not be as satisfactory as that possible with positive type resists, as indicated in figures 3 and 4. Various problems, perhaps not significant, have been encountered in using the negative type resist.

The stripe shaped texture observed in 8CB is a new layer-bend structure which differs from the chevron structure [11–13] and possibly is produced by a strong a.c. field with low frequency (< 10 Hz) applied to the chevron smectic layer or strong d.c. field applied to the SmA phase. The parallel layer structure appears wavy or as an in-plane zigzag, when viewed from above, in the plane parallel to the glass plate; chevron ridges run parallel to the glass plates in the chevron structure but perpendicular in the stripe texture [15]. The explanation for this is that when the length of any one side of an ultra-thin layer changes in response to external force, the length of the other side must also change under the condition of constant volume of a single layer. A low frequency a.c. field may shorten the layer length in the cell gap direction and this would cause the length of the layer parallel to the glass plate to increase, leading to in-plane zigzag. The electroclinic effect induced by a d.c. field application may thus reduce the layer spacing in the SmA layer [17]; layer length in the cell gap direction may then increase to give rise to the chevron structure as observed in chiral TM-C108 [12]. Stripes are not observed in the usual chevron structure; but if stripes were detected, an explanation for this would be that layers parallel to the glass plate would assume an in-plane zigzag structure since layer length in the cell gap direction cannot increase.

It would be of interest to determine which side of the layer changes in length in temperature gradient cooling. Layer spacing may possibly not change. If smectic layers take on the chevron structure, layer length in the cell gap direction may change. The chevron ridge, should it face left (C1-like deformation), may be pushed to the right by molecular movement and remain there (C2-like deformation). Deviation from the straight layer structure is very small at a layer tilt angle of 1–2·5° ($=\omega/2$) as observed in the previous section. Arch length decreases to give rise to an in-plane zigzag structure. However, this explanation is not applicable to the case of antiparallel rubbing where only stripe-shaped texture appears. The true mechanism by which achiral smectic liquid crystals display stripes without an external electric field should be clarified. The arrangement of stripe lines produced during temperature gradient cooling may differ from that of lines produced by the application of an electric field, as pointed out by Takanishi *et al.* [18].

5. Concluding remarks

The movement of molecules induced by temperature gradient cooling is a determinant of the layer structure of the SmA phase. A stripe-shaped texture is produced only when molecules move in the rubbing direction and appears in achiral smectic liquid crystals without the need for external electric field application. The dependence of the smectic layer structure formation on the direction of molecular movement or rubbing conditions is not readily evident in conventional cell structure with no narrow tunnels. Deformation of the SmA layer structure is remarkable for FLCs having a broad SmA temperature range and may be a primary determinant of the mode of SmA to SmC* phase transition. For FLCs with a SmA temperature range greater than 20°C, the structural change C1 → C2 does not occur and zigzag defects in C1 orientation are thus quite few in number. It may be possible to achieve the defect-free combination of C1 with C2 orientations by the use of such FLCs with multi-domain rubbing.

When considering orientation, including zigzag defects of smectic liquid crystals, the internal structure of the cell should also be taken into account. The cell is not simply a container as in the case of nematic liquid crystals.

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