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Surface Anchoring Stabilized High Strength Disclinations in Smectic C Phase of a Schiff-base Liquid Crystal†

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The observation of disclination cores of high strength $S=-2$, -3, -4, -5, -6, -7, -8 in a smectic C phase of Schiff-base type liquid crystal (LC) is reported. The results of polarizing optical microscope (POM), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) prove that the sample exhibits smectic C phase. It is suggested that the formation of the high strength disclination is mainly ascribed to the stronger anchoring of LC molecules on the substrate due to the formation of hydrogen bonds between the pendent hydroxyl of the LC molecule and the substrate.

Keywords high strength disclination, smectic liquid crystal, hydrogen bond

Introduction

Topological defects[1-4] in the distributions of the order parameter fields are extremely important objects of research in various of condensed-matter, such as superfluid helium 3 and 4,[5,6] crystalline solids,[7-9] liquid crystals,[10,11] and quantum Hall fluids.[12] Liquid crystals are ideal materials for studying topological defects.

Distortions yielding defects are easily produced through control of boundary conditions, surface geometries, and external fields. The resulting defects are easily imaged optically. The many different liquid crystalline phases (nematic, cholesteric, smectic-A, smectic-C, *etc*.) with different symmetry ground states make it possible to study different kinds of defects.

Schlieren texture in which a core bears several dark brushes is one of the typical textures of the liquid crystals which represents the defect of disclination.[13,14] The core does not change while the sample is rotated between the crossed polarizer and analyser, but the dark brushes rotate around the centre, indicating a continuous change in the direction of the optical axis. The dark brushes occur in areas in which director *n* of LC molecules is either parallel or perpendicular to the polarization plane of the incident beam. As follows from numerous observations[15-22] and theoretical studies,[23-28] two types of schlieren defects in nematics were reported, one is the simple planar disclination and the other is the complex disclination with a director curvature out of the plane. In the simple planar disclination, the revolution of the LC directors is limited in sample layer plane and possesses the following properties:

(1) The distribution of director around the defect is symmetrical.

(2) There is a simple relation between the strength *S* of the defect and the number *N* of dark brushes in the corresponding texture: $|S|=N/4$.

(3) High-strength defects ($|S|>1$) are prohibited in nematics, because a greater *S* implies a greater curvature of director *n* and, as a result, a greater elastic energy *F*.

According to Lavrentovich,[18,28] the complex disclination possesses an asymmetrical distribution of the LC director *n*, which includes the sectors with different *n* curvatures. In other words, the complex defect contains not only a planar radiallike distribution of director but also a director *n* revolution out of the layer plane.

The more number of the dark brushes emanates from a core, the more times the LC director revolution occurs around the core, therefore, the higher elastic distortional energy the core bears. Normally, only two or four extinguished brushes emanating from a core are observed, corresponding to the disclination strength $S=\pm 1/2$ and ± 1, respectively. There were a few reports on the observation of high strength disclination cores in low molecular weight LC[15-18] and in nematic liquid-crystalline polymers.[19-22] However, up to date, high strength disclinations have not yet been reported in smectic state. In this paper, the observation of stable singularity points of high strength in a smectic C phase is reported and the reason for which the high strength disclination arose and was stabilized is discussed.

Experimental

The samples were Schiff-base type liquid crystal *N*-[4-(undec-10-enoyloxy)-2-hydroxybenzylidene]-4-

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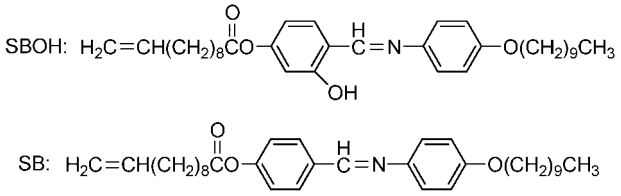
decyloxyaniline bearing pendent hydroxyl as well as *N*-[4'-(undec-10-enoyloxy)benzylidene-4-decyloxyaniline but not bearing pendent hydroxyl.



A Xintian XPID (China) polarizing microscope with a Metter FP-82 hot stage was used for texture observation. The cover slide was immersed in concentrated nitric acid for one day and then cleaned with water, alcohol and without any other modification. The differential scanning calorimetry (DSC) curves of the sample were recorded by a Perkin Elmer DSC 7 series system. And the temperature variable wide angle X-ray diffraction (WAXD) curves were recorded under a Rigaku D/max-r B with Cu target.

Results and discussion

Phase behaviour of SBOH

SBOH was sandwiched between two cover slide and observed between polarizer and analyzer. As shown in Figure l (a and b), one of the typical focal conic textures, the typical broken fan-like textures, and schlieren textures could be observed. When the up-cover slide was taken off and cooled from above isotropic temperature, the bubble texture which is one of the other focal conic textures could be observed as shown in Figure 1c. The texture observation shows that SBOH exhibits a smectic C phase.

Figure 2 shows the DSC heating and cooling traces of SBOH. On the heating scan (curve A), it shows a melting transition temperature (T_m) at 62 ℃ followed by a smectic C to isotropic phase transition at 127 ℃. The cooling scan (curve B) looks almost identical to the heating scan, except that a very small supercooling for the isotropic to smectic transition and a relative large one for the smectic C to crystal transition were observed.

The result of temperature-variable WAXD was also in agreement with the polarizing optical microscopic observation which is consistent with smectic C state. Figure 3 presents the temperature dependent X-ray diffraction diagrams obtained from the powder sample at 118, 110, 65 and 20 ℃. The diffraction patterns obtained at 118, 110, and 65 ℃ look almost the same. A broad reflection at wide angles (associated with the lateral packings) and a sharp reflection at low angles (associated with the smectic layers) could be observed on the above curves. Only the *d*-spacings are different. The layer spacing increases with decreasing the temperature.

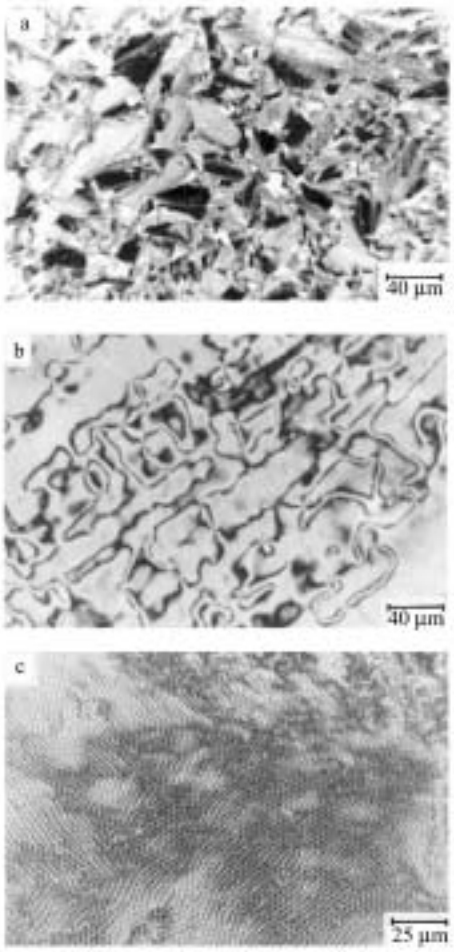


Figure 1 Textures of SBOH between crossed polarizers. (a) broken fanlike texture; (b) schlieren texture; (c) bubble texture.

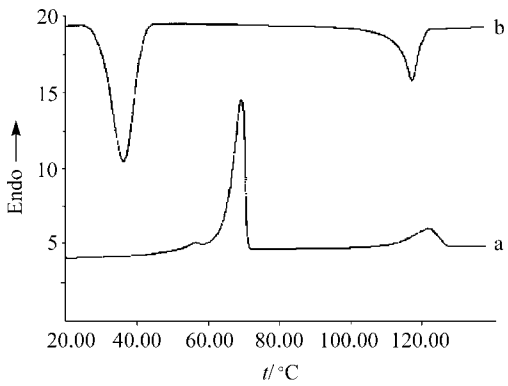


Figure 2 DSC curves of SBOH. (a) heating scan; (b) cooling scan.

Phase behaviour of SB

The phase behaviour of SB was similarly studied. The POM, DSC and WAXD results indicate that SB exhibits smectic C phase from 78 to 96 ℃ and smectic A phase from 96 to 111 ℃.

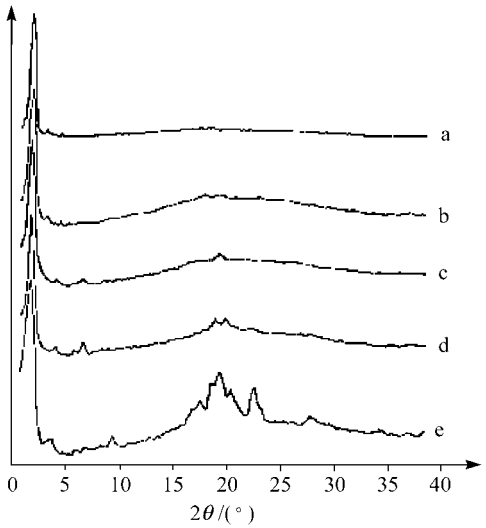


Figure 3 WXRD diagram of SBOH at different temperature. (a) 118 ℃; (b) 110 ℃; (c) 65 ℃; (d) 20 ℃; (e) 15 ℃.

High strength disclinations

When the up-cover slide was carried off, disclination cores bearing many dark brushes were easily observed for SBOH while such cores were not observed for SB even upon a more careful observation.

A detailed observation of the defects by using a sensitive colour plate and a quartz wedge under polarizing microscope indicated that the high strength disclination cores observed in SBOH are the simple planar disclination in which the revolution of the LC director is limited in the sample plane. Near the isotropization temperature of SBOH, the forming process of the high strength cores was observed. When the sample changed from isotropic to anisotropic state, some "dark bands" were formed as well as many cores of strength $|S|=1$ at the two phase existing area, and there were many dark brushes on the dark band, especially on its end (as shown in Figure 4a). When the dark band contracted, the density of the brushes on it was increased. Finally, when the dark band contracted to an point-like area, the brushes were arranged around it, and a disclination core of high strength was formed as shown in Figure 4 (b, c and d). The entire process took several seconds. The dark band does not change while the crossed polarizers are rotated. It is inferred that the dark band is an isotropic area, and the core of high strength formed from the dark band is also an isotropic area.

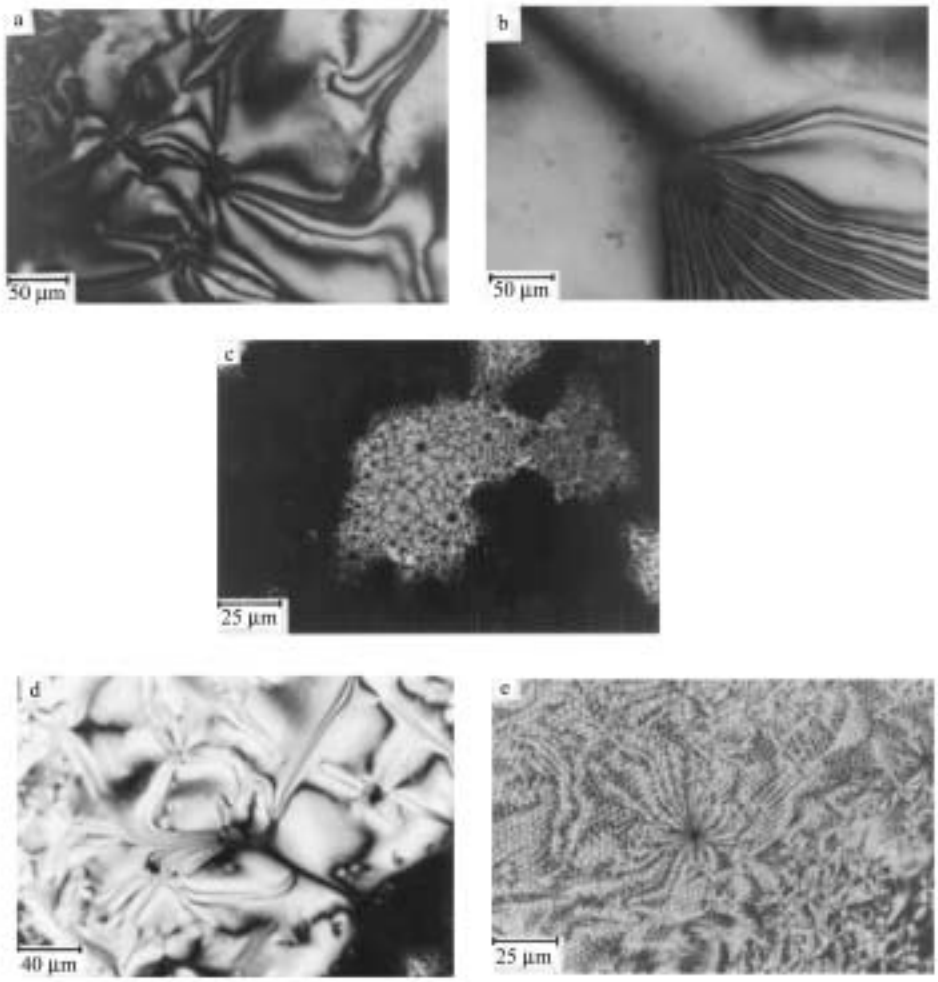


Figure 4 Forming process of the high strength disclinations in SBOH. The dark band bearing many brushes contracted to a core of high strength disclination.

The cores bearing 12 brushes appear, corresponding to the disclination strength with $|S|=3$ (Figure 4a). The singularity has twenty four dark brushes, corresponding to the disclination strength with $|S|=6$ (Figure 4b). As shown in Figure 4c, at least two cores each bearing eight brushes, three cores each bearing twelve brushes, four cores each bearing sixteen brushes, two cores each bearing twenty brushes, one core bearing twenty four brushes and one core bearing twenty eight brushes could be observed, corresponding to the $|S|=2$, 3, 4, 5, 6 and 7, respectively. Paired high strength defects, made of one defect with a strength of $|S|=7$ with twenty eight brushes and the other of $|S|=4$ with sixteen brushes were found (Figure 4d).

The high strength cores originally formed were unstable, and their strength changed because they merged or split. But some of the high strength cores moved to the thicker area of the film. As the temperature slightly decreased from the isotropization temperature, the bubble texture of smectic phase was formed and the cores were surrounded by bubble textures and stabilized (as shown in Figure 4e). These high strength cores were stable enough to exist for several tens of minutes if the sample was maintained at proper temperature. The singularity shown in Figure 4e has thirty two dark brushes. When rotating the hot stage, the brushes rotated at the same direction as the hot stage, and its strength could be inferred to -8. It is noted that the rotation rate of the dark brushes is much slower than that of the stage.

When the up-cover slide was carried off, the thickness of the film formed on the glass slide was not equal on the different area of the slide. At the thinner area, many cores of high strength were observed (Figure 5). As shown in Figure 5 (a and b), the cores bearing 24 and 16 brushes were observed, corresponding to the disclination strength $|S|=6$ (Figure 5a) and 4 (Figure 5b), respectively. When rotating the hot stage, the dark brushes of all the high strength cores rotate at the same direction as the hot stage, hence their strength $S=-6$ (Figure 5a) and -4 (Figure 5b), respectively. As shown in Figure 5c, at least four cores each bearing 8 brushes could be observed and also the cores each bearing 12, 16, 20 or 24 brushes could be observed. The singularity shown in Figure 5d has 8, 12, 16 and 20 dark brushes. As the same as the cores observed in Figure 5 (a and b), the disclination cores in Figure 5 (c and d) are also negative. Of course, it is necessary to distinguish between true high-strength disclinations or several dark brushes bunched together from other neighbouring cores. If multiple dark brushes of a schlieren texture could break up sometimes from a core as the hot stage rotated, it is not a real high-strength disclination. Otherwise, as the hot stage rotated, the numbers of dark brushes (32 in Figure 4e and 24 in Figure 5a and 16 in Figure 5b and 8, 12, 16, 20 and 24 in Figure 5c and 8, 12, 16 and 20 in Figure 5d) were constant, and brushes rotated continuously in the same (negative *S*) sense around a core.

Unlike the high-strength cores previously observed,[2,4] these disclination cores are stable. The cores we observed in the thinner area of the film were more stable than those observed in the thicker area. The singularity points of high strength as shown in Figure 5 were stable enough to exist longer than an hour while the sample was maintained at 100 ℃. They were

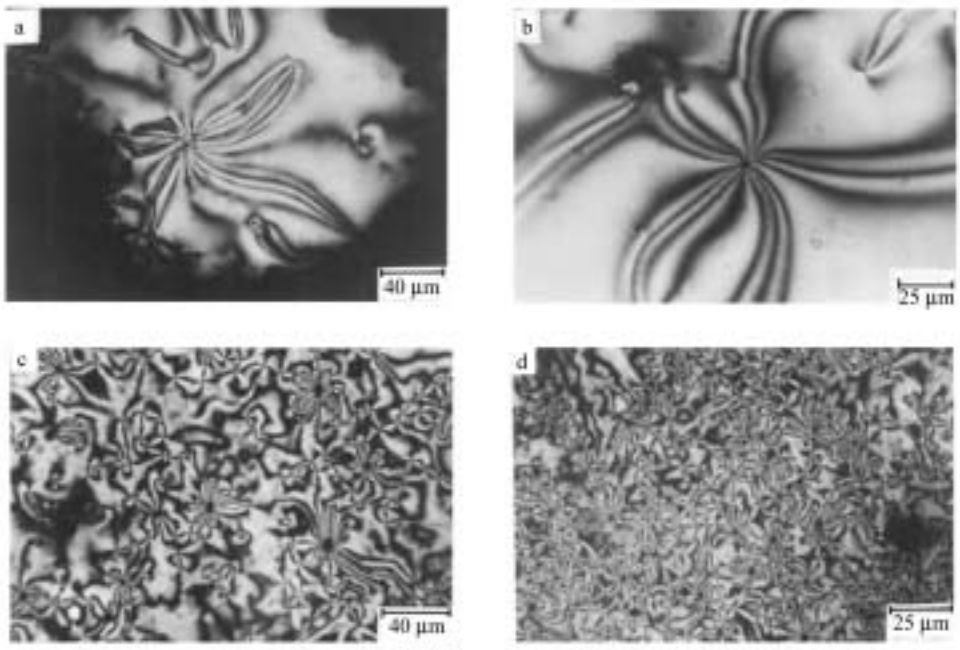


Figure 5 Disclination cores of different strength formed at the thinner area of the preparation of SBOH.

damaged until the temperature decreased to the crystalline temperature of the sample (62 ℃).

It is necessary to discuss the reason for that the high strength disclination arose and was stabilized. Zhou *et al.*[21] suggested that the wider core of the disclination might have the function of releasing partially the stress generated by the greater number of turns of the molecular directors about a defect with higher strength and is thus helpful to the stabilization of the high strength disclination. We suggested that the high strength disclination observed here is ascribed to the pendent hydroxyl group of the sample. The hydrogen bond may be formed between the pendent hydroxyl groups of SBOH and surface of the glass substrate of cover slide. Therefore, there will be a more stronger anchoring of SBOH than that without a hydrogen bonding action (as shown in Figure 6). Above the clearing point of the sample the liquid crystal molecules were bound to the substrate surface disorderly. With the decreasing of the temperature, many domains in which the liquid crystal molecules had different alignment were formed, the domains met to each other and the alignment direction of the liquid crystal molecules had to be merged. But because the liquid crystal molecules had a stronger anchoring to the substrate, many of the turns of the director arose and the high strength disclinations were easily formed.

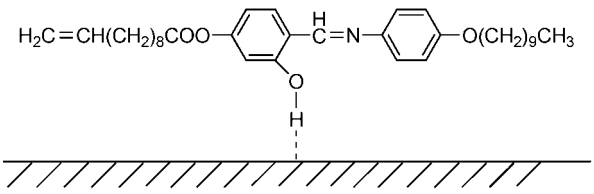


Figure 6 Stronger anchoring of SBOH on the substrate due to the formation of hydrogen bonds between pendent hydroxyl and the substrate.

As mentioned before, the high strength disclination cores can not be observed for SB which does not bear a pendent hydroxyl group even upon more careful observation. It proves that the hydrogen bonding action between the substrate and the sample is a main reason for that the high strength disclination cores arise.

The hydrogen bonding action between the liquid crystal molecules and the surface is also helpful to the stabilization of the high strength disclination. The anchoring of the sample bearing pendent hydroxyl group is much higher than that of the general liquid crystals without a pendent hydroxyl. Therefore, the high strength disclinations were easily observed and has a much more stability. It is observed that the high strength disclination in the thinner area has a higher stability than in the thicker area. It indicated a competition between the surface anchoring and the bulk assembling of the liquid crystal. The effect of the surface anchoring at the thinner area is stronger than that of the bulk assembling of the liquid crystal. Therefore, the high strength disclination at the thinner area has a much higher stability. On the other hand, the viscosity of smectic liquid crystal is greater than that of the nematic liquid crystal. The higher viscosity is also helpful to the stabilization of the high strength disclination. The high strength disclination formed around clearing point was frozen in the smectic C phase with a higher viscosity when the temperature decreased.

In conclusion, the stable high strength defects with 8, 12, 16, 20, 24, 28 and 32 dark brushes, corresponding to strength of $S=-2$, -3, -4, -5, -6, -7 and -8 were observed in a smectic C phase of single-component small-molecule liquid crystal of Schiff-base type with *o*-hydroxyl. Their high stability can be ascribed to the pendent hydroxyl group of the sample and their high viscosity.

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