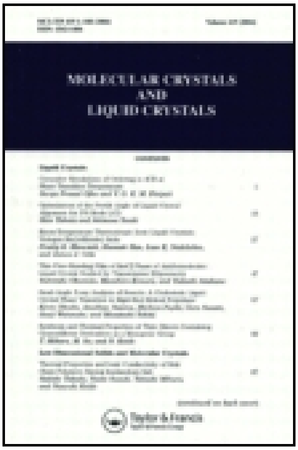

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Microscopic Study on the Molecular Arrangements in the Smectic A, B and C Modifications

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Microscopic Study on the Molecular Arrangements in the Smectic A, B and C Modifications

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Abstract—The molecular arrangements in three smectic modifications, i.e., the smectic A, B and C states are discussed on the basis of optical observations of smectic spherulites, which were fixed in a very viscous polymer matrix. The observed microscopic patterns for the smectic A state support the conventional idea that the smectic A state has a molecular arrangement such that the long molecular axis lies perpendicular to the layers. In the smectic B state, similar patterns to the smectic A were observed, suggesting a similar molecular arrangement to the smectic A state. On the other hand, the smectic C state exhibits strikingly different patterns from those of the smectic A and B states. Twisted smectic layers are proposed for the molecular arrangement of the smectic C state in order to reasonably explain all the observed microscopic patterns.

1. Introduction

Sackmann, Demus and Arnold have indicated from their optical studies on the smectic mesophase that this mesophase can be further classified at least into three different types which are denoted by A, B and C.(1–6) According to recent studies the smectic A phase has been interpreted to have a molecular arrangement such that the long axes of the molecules lie approximately perpendicular to the smectic layers and there is no order within a layer.(7) The detailed molecular arrangements in the smectic B and C phases still remain unknown, although it is suggested that the smectic B and C phases have higher ordered structures since they always occur at a lower temperature than the smectic A.(8,9)

In order to get information on the difference in the molecular arrangement among these three smectic phases, microscopic observations were carried out with smectic spherulites which were fixed in the matrix of a very viscous polymer and remained stable as the spherical body over the temperature range of the smectic mesophase. Use of such a stable spherical body makes it possible to observe in detail the microscopic patterns and to discuss the molecular arrangement in the smectic state.

2. Experimental

All microscopic observations were made using a Nikon POH polarizing microscope between crossed polaroids and the liquid crystal specimens in polymer matrices were heated on a heating block mounted on the rotating stage. A sensitive color plate (R = 530 mμ) was used as a test plate to determine interference colors. The temperature of the sample was measured using chromel-alumel thermocouples.

Smectic liquid crystal compounds used in this study are as follows; *p*-*n*-octyloxybenzoic acid (OOBA), *p*-*n*-octadecyloxybenzoic acid (ODOBA), ethyl-*p*-(4-ethoxybenzylideneamino-)cinnamate (EEBAC) and *p*-*n*-decyloxybenzylidene *p*-toluidine (DOBT). With the exception of OOBA obtained commercially from Tokyo Kasei Co., all the compounds were synthesized in our laboratory, and purified by successive recrystallization from hot ethanol. The transition temperatures for these compounds are compiled in Table 1.

In order to obtain the stable smectic spherulites, a mixture of liquid crystalline compound and polymer matrix (epoxy cement) was prepared and heated to give the isotropic liquid state of the compound

TABLE 1 Transition Temperatures of Compounds Studied

Sample	smectic B	smectic C	smectic A	nematic	isotropic
p-*n*-Octyloxybenzoic acid		101		108	145
p-*n*-Octadecyloxybenzoic acid		103			131
p-*n*-Decyloxybenzylidene *p*-toluidine	(64)		70	78	79
Ethyl-*p*-(4-ethoxybenzylideneamino-) cinnamate	78		115	155	157

( ): Monotropic (cooling only)

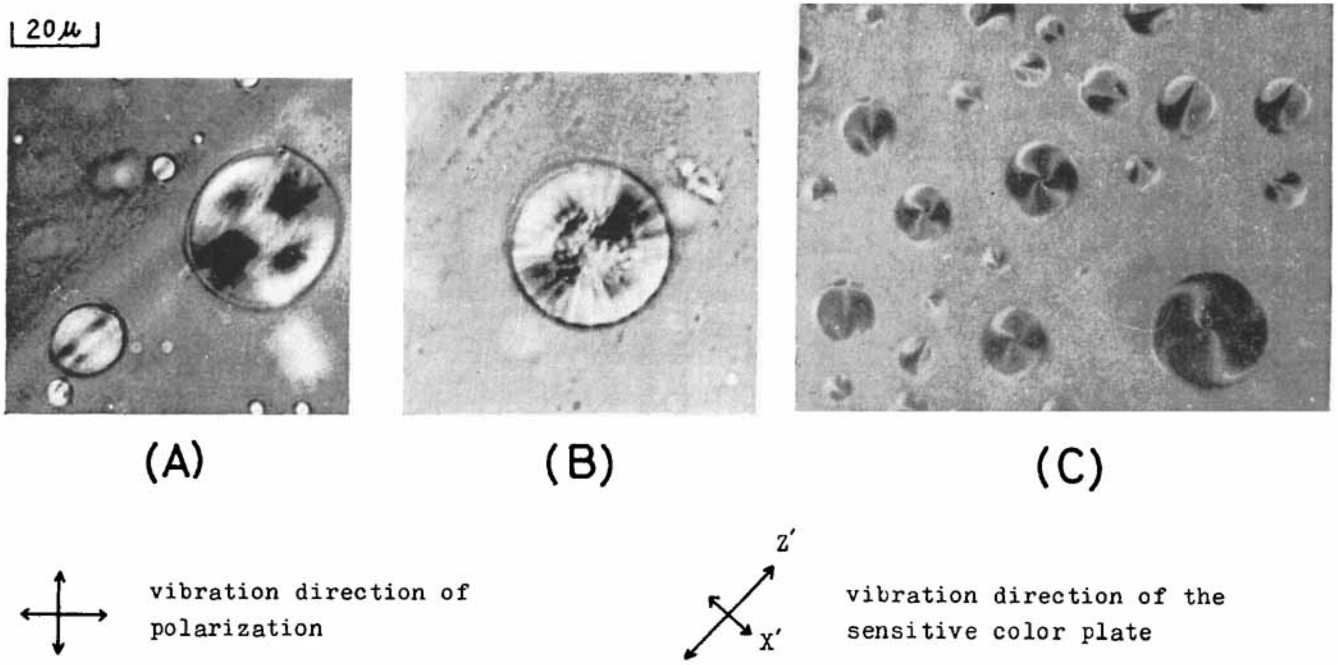

Figure 1. Typical microscopic patterns observed in the smectic A, B and C spherulites: (A) the smectic A, (B) the smectic B, (C) the smectic C.

between a glass slide and a cover slip on the microscopic stage with the heating block, and then cooled slowly in order to obtain the smectic mesophase. In such a matrix the smectic spherical bodies are not free to move and to coalesce with each other over the temperature range of the mesomorphic state. The stable mesomorphic spherulites in the matrix were measured to be several to a few tenths microns in diameter.

3. Results

Fig. 1 shows the photographs of the patterns observed in the smectic A, B, and C spherulites.

3.1. EEBAC AND DOBT

EEBAC exhibits two smectic mesophases, namely smectic A and B phases.(3,13) The microscopic observation and the differential thermal analysis show that DOBT also exhibits these two smectic mesophases although the smectic B state is monotropic with respect to the crystalline state. The microscopic patterns observed for these smectic A and B phases are illustrated in Fig. 2 and Fig. 3, respectively. Figure 2 shows the patterns of the smectic A phase observed for both of the above liquid crystal compounds. Smectic spherulites surrounded completely by the highly viscous polymer matrix which eliminates substantially the influence of the glass surface give either the pattern (a) or (b), while the spherulites which adhere to the glass

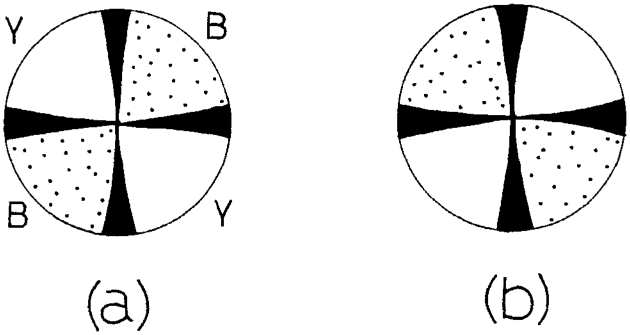

Figure 2. Two typical patterns observed in the smectic A state. Dotted area shows blue interference color and unmarked area shows yellow.

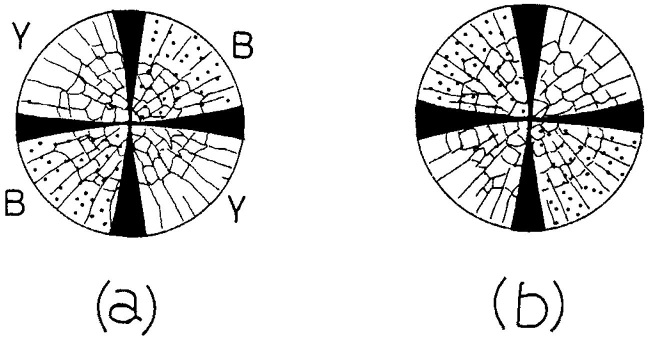

Figure 3. Schematic representation of the microscopic patterns observed in the smectic B state.

surface show mostly the pattern (a). These two patterns in the smectic A state have identical sharp isogyres with each other, which are invariant on rotating the microscopic stage if one disregards the reverse of interference colors in the quadrants.

Figure 3 shows the patterns obtained for both of those compounds in the smectic B state. Again, both the sharp isogyre and interference color remain unchanged, as in the case of the smectic A state, with respect to the rotation of the stage. The patterns observed for the smectic B are very similar to those of the smectic A, except that many cracked lines are observed over the whole smectic spherulite. Those cracks are observed only for the smectic B state and appear to be characteristic of this mesophase.

3.2. OOBA AND ODOBA

OOBA produces both the nematic and smectic mesophases, while ODOBA gives only the smectic mesophase.(10,11) However, the smectic state of these compounds is concluded to be the smectic C mesophase since it exhibits the smectic schlieren texture when observed under a polarizing microscope.(5,12) Figure 4 shows typical microscopic patterns observed for the smectic C phase of these compounds. In these patterns the sharp cross of extinction does not emerge at all and the regions of extinction are characteristically curved. Furthermore, the isogyre of the type C(I) in Fig. 4 is invariant on rotating the stage of the polarizing microscope, whereas that of the type C(II) varies successively through 360° when the

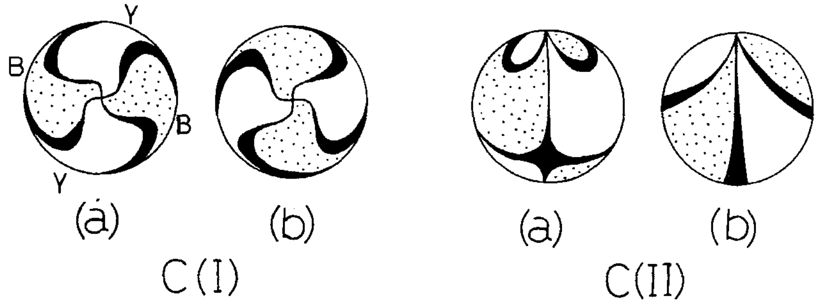

Figure 4. Two groups of typical patterns observed in the smectic C state.

stage is rotated, as illustrated in Fig. 5. In the case of type C(I), the centric region of the spherulite shows a yellow interference color in the first and third quadrants and blue in the second and fourth quadrants.

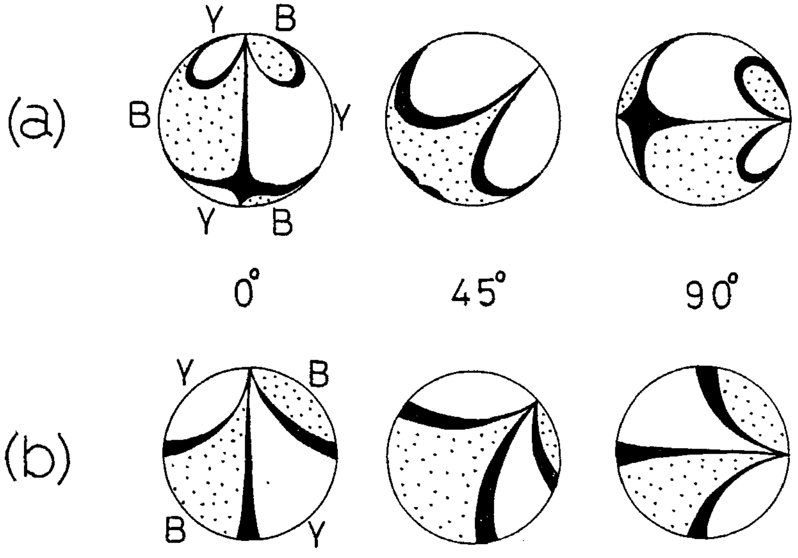

Figure 5. The changes of the pattern C(II) on rotating the stage of the microscope.

4. Discussion

Two typical microscopic patterns observed for the smectic A state (Fig. 2) indicate that the molecules are arranged in concentric circles about the center of the spherulite or radiate from the center, as shown in Fig. 6. The pattern (a) in Fig. 2 can be obtained if the molecules in the spherulite are arranged in the same manner as those in the model (a) shown in Fig. 6. In this model, the long molecular axes in the first and third quadrants coincide with the vibration direction of the extraordinary ray in the test plate, leading to an increase in the retardation which dominates the interference color. Therefore, the interference color becomes blue in the first and third quadrants while yellow in the second and fourth quadrants. Moreover, it is apparent that the extinction positions in this model are invariant with respect to the rotation of the stage. Therefore, it can be expected that the smectic A state which gives the pattern (a) in Fig. 2 has the molecular arrangement similar to that shown in the model in Fig. 6(a). The observed pattern (b) can be also related to the smectic spherulite with a molecular arrangement of model (b) in Fig. 6. It should be noted, however, that two proposed models concerning molecular arrangements in the smectic A state are more likely associated with each other, because a small part of the spherulite in both models holds the essentially identical molecular orientation, that is, the long molecular axis perpendicular to the layer. Hence, both models proposed as the molecular arrangement in the smectic A state are consistent with a conventional idea that the smectic A state has such a structure that the molecules are arranged in layers with the long molecular axis perpendicular to the layer.

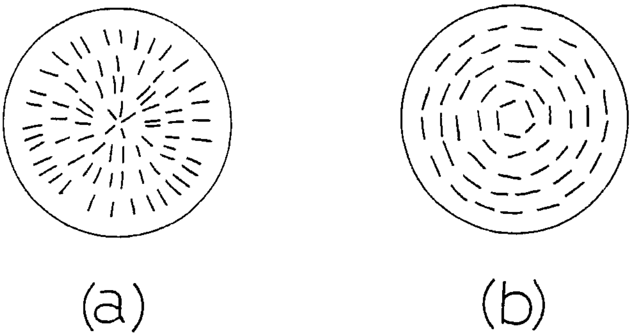

Figure 6. Schematic molecular arrangement corresponding to two typical smectic A patterns. The full lines indicate the directions of the long molecular axes.

The difference in two molecular arrangements shown in Fig. 6 may be mainly due to the influence of the glass surface and polymer matrix.

The smectic B state exhibits similar microscopic patterns to those of the smectic A state, except that many cracked lines are observed in the spherulites, and can be, therefore, expected to have molecular arrangements similar to those of the smectic A state. These cracks develop near the transition temperature in going from the smectic A state to the smectic B state and disappear completely in the crystalline state. Furthermore, for EEBAC which enantiotropically exhibits both the smectic A and B states, such cracks were observed both on heating and cooling in spite of different textures. These facts lead to the conclusion that these cracks are attributed not to the environmental effect of the polymer matrix but to essential properties of the smectic B phase. Furthermore, it can be also suggested from the observed behavior of the sharp isogyre and of the interference color figure that in the smectic B state there are no curved layers.

The smectic B state has so far been considered to have the molecular axis perpendicular or tilted to the layer in which there exists a further molecular order. Levelut and Lambert have also assumed a smectic hexagonal structure for the smectic B state.(8) Arnold has reported from calorimetric measurements that the heat capacity changes considerably at the transition between the smectic modifications B and A of EEBAC.(13,14) Such large transition heats would correspond to a clear difference in the molecular arrangement between smectic A and B phases. The characteristic cracks observed in the smectic B state may be essentially ascribed to the change of a molecular arrangement within the layer. However, it remains still ambiguous whether the cracks can be ascribed to the change in the molecular order within the layer or to other origins. At present this can not be referred to in further detail, although it may be considered that the cracks are likely associated with the very high viscosity of the smectic B phase.

A comparison between the microscopic patterns shown in Fig. 2 and Fig. 4 indicates definitely that the molecular arrangement in the smectic C state differs strikingly from that in the smectic A. Sharp isogyres are not observed at all for this smectic C state and the regions of extinction are characteristically curved, as seen from Fig. 4 and Fig. 5. The pattern C(I) in Fig. 4 is invariant on rotating the stage while the pattern C(II) changes successively as illustrated in Fig. 5. These curious observations for the smectic C state can not be explained using molecular arrangements similar to those found in the smectic A state. So far the smectic C state has been recognized as having a tilted smectic layer.(15,17) But, the curved isogyre can not be reasonably explained by this tilted smectic layer. In order to explain the curved isogyre and its behavior with respect to the rotation of the stage, we can assume more reasonably twisted smectic layers which are schematically illustrated in Fig. 7 as the molecular structure in the smectic C state. In this model, the molecules are arranged in layers with the long molecular axis successively twisted with respect to the layer normal. In other words, the direction of the long axes of the molecules varies helicoidal. Assuming such twisted smectic layers, the observed microscopic patterns for the smectic C state can be easily explained. The invariant pattern C(I) is attributed to smectic spherulites in which the helicoidal axis is perpendicular to the plane of the stage, and the emergence of the characteristically curved isogyre can be easily analyzed by the model for molecular arrangement proposed in Fig. 8. With this model it can be also understood without any difficulty that in the centric regions of two patterns, the interference color is yellow in the first and third quadrants, and blue in the second and fourth quadrants. On the other hand, the helicoidal axis of the pattern C(II) illustrated in Fig. 4 must lie approximately parallel to the plane of the stage.

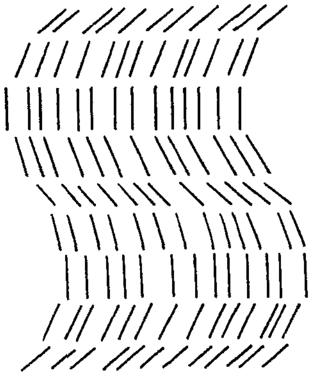

Figure 7. Schematic representation of the twisted smectic layers.

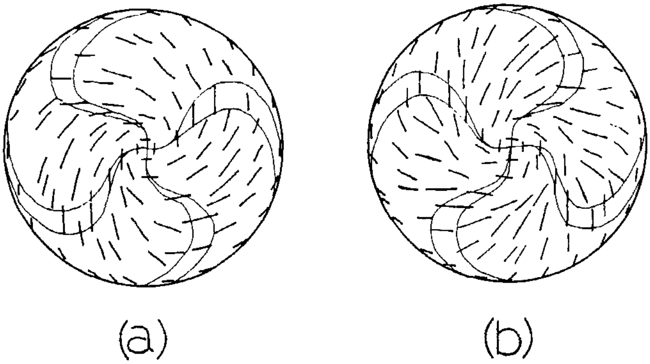

Figure 8. Schematic representation of the molecular arrangement corresponding to the pattern C(I) in Fig. 4. The curved lines indicate the extinction contours.

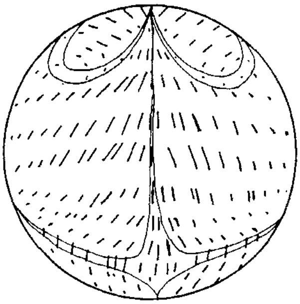

Figure 9. Schematic representation of the molecular arrangement corresponding to (a) of the pattern C(II) in Fig. 4.

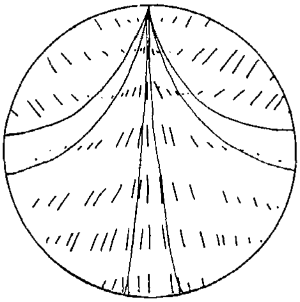

Figure 10. Schematic representation of the molecular arrangement corresponding to (b) of the pattern C(II) in Fig. 4.

Figures 9 and 10 show the model of the molecular arrangement corresponding to the observed pattern C(II) in Fig. 4. The change of the pattern on rotating the microscopic stage can be also explained by the twisted smectic layers.

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