Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: Kazuaki Wagatsuma, Aritada Hatta & Wataru Suëtaka (1979): Application of Infrared ATR Spectroscopy to Liquid Crystals. III, Molecular Crystals and Liquid Crystals, 55:1, 179-192

To link to this article: http://dx.doi.org/10.1080/00268947908069801

Mol. Cryst. Liq. Cryst., 1979, Vol. 55, pp. 179–192
0026-8941/79/5501-0179$04.50/0

Printed in United States of America

Application of Infrared ATR Spectroscopy to Liquid Crystals. III.

Molecular Reorientation of Nematic EBCA in a DC Electric Field

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(*Received April 30, 1979; in final form June 6, 1979*)

Infrared absorption measurements of nematic N-(*p*-ethoxybenzylidene)-*p*′-cyanoaniline (EBCA) under a DC electric field were performed by means of our previously reported ATR method. DC voltages up to 15 V were applied to the nematic liquid crystal 15 μm thick between a silicon ATR prism (probing electrode) and an In_2O_3-coated glass electrode (opposite electrode). By using this method the orientational behavior of molecules in boundary layers about 1 μm thick at the Si electrode was investigated.

The threshold voltage for the dielectric orientation varied from 2 to 6 V depending upon the boundary conditions at the opposite electrode, and the maximum degree of order of homeotropic orientation was found to be 0.6–0.7. A storage effect, in which a homeotropic texture induced by the electric field remains unaltered even if the field is removed or reversed, was observed.

INTRODUCTION

Considerable interest has recently converged to the electro-optical properties of liquid crystals because of their potential utility as light modulators or information display devices.[1] For example, a homogeneous DC electric field can exert an orienting influence through the dielectric anisotropy upon a nematic liquid crystal, and thereby the optical properties change because of the refractive anisotropy of the constituent molecules.

Various methods have been introduced for the study of the electro-optical properties of liquid crystals, but much has been concerned with the measurements of dielectric anisotropy or birefringence. For obvious reasons, however, more direct information on molecular orientation under the influence of DC electric field, which should be obtained by infrared spectroscopy, is of importance as well. Infrared spectroscopy has widely been used for investigating liquid crystals, but little has been performed on electric field-induced orientation.

Neff *et al.* have measured the molecular orientation of bulk nematic N-(*p*-methoxybenzylidene)-*p*′-cyanoaniline in a DC electric field using a transmission absorption method.[2] They obtained a homeotropic orientation with a maximum degree of order of 0.33. However, the observation of the depressed degree of order suggests that the interaction between liquid crystal molecules and electrode surfaces lowered the response of liquid crystal to the electric field. Such a surface effect is of considerable interest for both fundamental and applied researches.

Apart from the study of the bulk liquid crystal, numerous possibilities are opened up in the way of liquid crystal investigations using the infrared ATR technique employed in our laboratory.[3] Unlike the transmission technique, the ATR method is capable of giving absorption spectra of boundary layers of liquid crystal molecules at the ATR prism surface. From the absorption data new information has been obtained concerning the dynamic scattering and dielectric orientation of MBBA molecules.[4]

In the present paper, we desribe the ATR results of dielectric orientation of nematic N-(*p*-ethoxybenzylidene)-*p*′-cyanoaniline (EBCA) having a positive dielectric anisotropy.

EXPERIMENTAL

For the measurements of polarized ATR spectra, the optically balanced double-beam attachment was mounted in a JASCO IR–G grating spectrophotometer equipped with a AgCl polarizer. The sample and the reference beams were incident upon the internally reflecting interfaces of Si prisms at 40° with an estimated angle of convergence of 2°.

The temperature-controlled liquid crystal cell has already been described.[3] The liquid crystal film 15 μm thick was placed between the silicon prism and an In_2O_3-coated glass plate both of which served as electrodes; a DC electric field was applied normal to the liquid film.

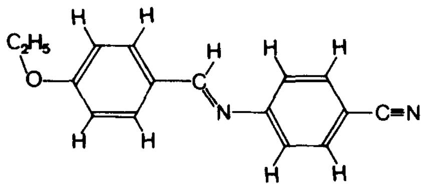

FIGURE 1 The structure of EBCA.

Guaranteed-grade EBCA from Tokyo Chemical Industry Co. was used without further purification. The structure of EBCA is shown in Figure 1. EBCA is nematic in the range 105.5–128.9°C.[5]

METHOD

According to the treatment by Saupe and Maier, the degree of orientational order of nematic liquid crystals is defined by[6]

$$S = \tfrac{1}{2}\langle 3\cos^2\alpha - 1\rangle, \tag{1}$$

where α is the angle between the long axis of the molecule and the optical axis, and the brackets denote an average over the orientation of all molecules. Obviously, the precise distribution of molecules cannot be determined from infrared measurements. Nevertheless, polarized infrared light can serve as a tool for evaluating an average direction of transition moment of vibration with respect to the optical axis of the nematic liquid crystal. In this case we suppose that the molecular long axes are displaced by a common angle α from the optical axis. In addition if we assume the molecules to rotate freely around their long axes, the degree of order is then simply expressed by[3]

$$S = \frac{(d-1)}{S_\beta(d+2)}, \tag{2}$$

where $S_\beta = (3\cos^2\beta - 1)/2$ and the angle β is measured between the long axis and the direction of the transition moment involved. Furthermore, d is the dichroic ratio defined as $K_\parallel/K_\perp$, where $K_\parallel$ and $K_\perp$ are the absorption coefficients for radiation polarized parallel and perpendicular to the optical axis, respectively. In this definition any orientation can be indicated by positive S values which may extend to a limit of unity.

According to Eq. (2) the angle of inclination β for any particular vibration permits an evaluation of S from the measured dichroic ratio. Actually the majority of infrared study of order parameter determination has been made along this line, but confined to the use of a conventional transmission technique. The transmission technique, however, has an inherent difficulty in that no information along the direction of wave propagation is obtainable generally. In the ATR method, on the other hand, one measures the reflection loss due to the interaction of absorbing medium with an evanescent wave whose electric fields exist in three directions at the reflecting interface.[7]

Figure 2 shows a total reflection system in which a Si prism and an anisotropic liquid crystal are in contact with each other at an optically flat boundary between them. The infrared radiation is incident upon the liquid crystal

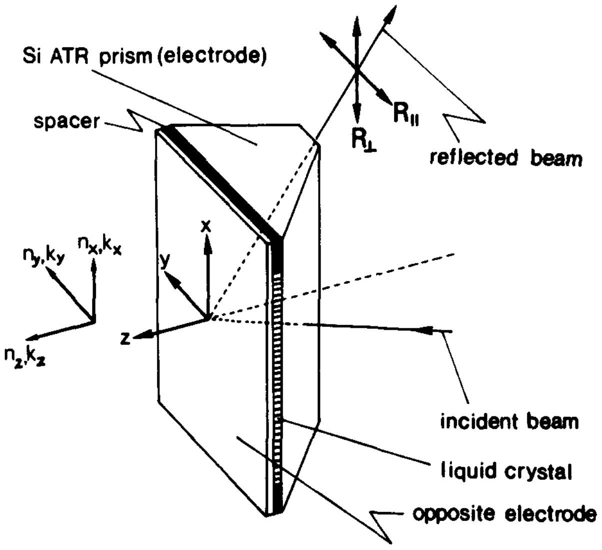

FIGURE 2 Geometry of liquid crystal cell and coordinate system for the attenuated total reflection (ATR). $R_{\parallel}$ and $R_{\perp}$ indicate the reflectivities of the radiation polarized parallel and perpendicular to the plane of incidence (yz plane), respectively.

whose thickness is much greater than the penetration depth of evanescent wave.[8] For a definite angle of incidence that is larger than the critical angle of total reflection, the amount of reflection loss depends upon the complex refractive indices of the liquid crystal which are given by $\hat{n}_j = n_j(1 + ik_j)$, where n_j and k_j are, respectively, the real part of the refractive index and the extinction coefficient along the j axis (see Figure 2). The remainder of the quantities which contribute to the reflection loss is the refractive index of the Si prism.

For small k_j values, *i.e.*, $k_j < 0.1$, the logarithm reflectivities for polarized radiations with the electric vectors perpendicular and parallel to the plane of incidence are[9]

$$\ln R_{\perp} = -pk_x \tag{3}$$

and

$$\ln R_{\parallel} = -qk_y - rk_z, \tag{4}$$

where p, q, and r are functions of the refractive indices of the absorbing medium and of the internal reflection prism. It is desirable to know accurately the refractive indices of the liquid crystal which alters in changing the degree of order. However, the birefringence of liquid crystals so far reported has been limited to the visible region and not yet measured in the infrared region. We shall therefore assume that the birefringence is much smaller in the infrared region than in the visible region.[3] The n_j value can safely be approximated by the ordinary refractive index obtained with the visible light.

For a practical analysis, it is convenient to introduce a dichroic ratio which is defined as

$$D = \frac{\ln(R_{\parallel}^{\circ}/R_{\parallel})}{\ln(R_{\perp}^{\circ}/R_{\perp})}, \tag{5}$$

where $R_{\parallel}^{\circ}$ and $R_{\perp}^{\circ}$ are the background reflectivities of radiation polarized parallel and perpendicular, respectively, to the plane of incidence. Then we can write

$$D = \frac{q}{p}\left(\frac{K_y}{K_x}\right) + \frac{r}{p}\left(\frac{K_z}{K_x}\right). \tag{6}$$

In this expression the extinction coefficients k_j in Eqs. (3) and (4) were replaced by the associated absorption coefficients K_j. Using the uniaxial model for nematic liquid crystals, Eq. (6) becomes simpler in some special cases. For instance if the molecules are uniformly oriented parallel to the x axis (see Figure 2) one has

$$D = \frac{q + r}{p}\left(\frac{1}{d}\right), \tag{7}$$

where $d = K_x/K_y = K_x/K_z$.

One should note that if the molecules are randomly oriented the value of dichroic ratio becomes $D = (q + r)/p$ for any types of vibration. Thus, if the values of p, q, and r are known, the experimental D value, and therefore d value is available for determining the degree of order.

Using the refractive index 3.42 for the Si prism[10] and $n_j = 1.57$ assumed for EBCA,[11] we obtain $p = 1.82$, $q = 1.27$, and $r = 2.60$. Here the n_j value is only approximate but the small variation of this term is not so sensitive to the quantities of q/p and r/p, and does not lead to serious errors in the resulting S value.

RESULTS AND DISCUSSION

Transmission spectra

Our interest is focused mainly upon the C≡N stretching as an indicator of the EBCA orientation. As mentioned above an *a priori* knowledge of the β value of the C≡N stretching is required. Polarized transmission measurements of a uniformly oriented sample were used as an aid in the determination of the β value. The oriented sample was obtained by a conventional rubbing technique as reported before.[3]

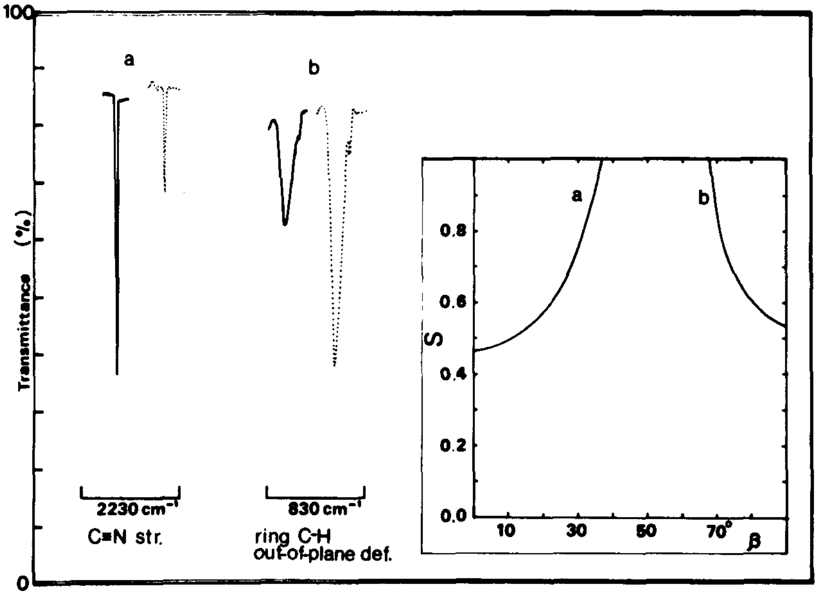

FIGURE 3 Polarized transmission spectra of a uniformly oriented EBCA (left) and the degree of orientational order (S) as a function of deflection angle (β); a: 2230, b: 830 cm^{-1}. Solid and dotted lines refer to the electric vectors of radiation parallel and perpendicular to the optical axis (rubbing direction).

Figure 3 shows the spectra of the C≡N stretching and the phenyl C—H out-of-plane deformation. The full and dotted lines refer to the electric vectors of radiation polarized parallel and perpendicular to the rubbing direction, respectively. Assuming that the optical axis coincides with the rubbing direction, the dichroic ratio of the C≡N stretching is obtained to be $d = 3.59$. In contrast $d = 0.37$ is obtained for the band of the phenyl C—H out-of-plane deformation. Such the great difference in dichroic ratio definitely shows that the former vibration has its transition moment nearly parallel to the optical axis while the latter perpendicular to that axis. The S values estimated from Eq. (2) using the dichroic ratios obtained were plotted as a function of β. The results are inserted in Figure 3.

From the figure, the β values of the C≡N stretching and of the phenyl C—H out-of-plane deformation are obtained concurrently against a specified value of S. In the absence of further information available for determining the S value, however, the β value of the C≡N stretching remains undetermined. Then we assume that the transition moment of the phenyl C—H out-of-plane deformation is perpendicular to the long axis of the molecule, *i.e.*, $\beta = 90°$. The S value is found from Figure 3 to be 0.53. From Eq. (2)

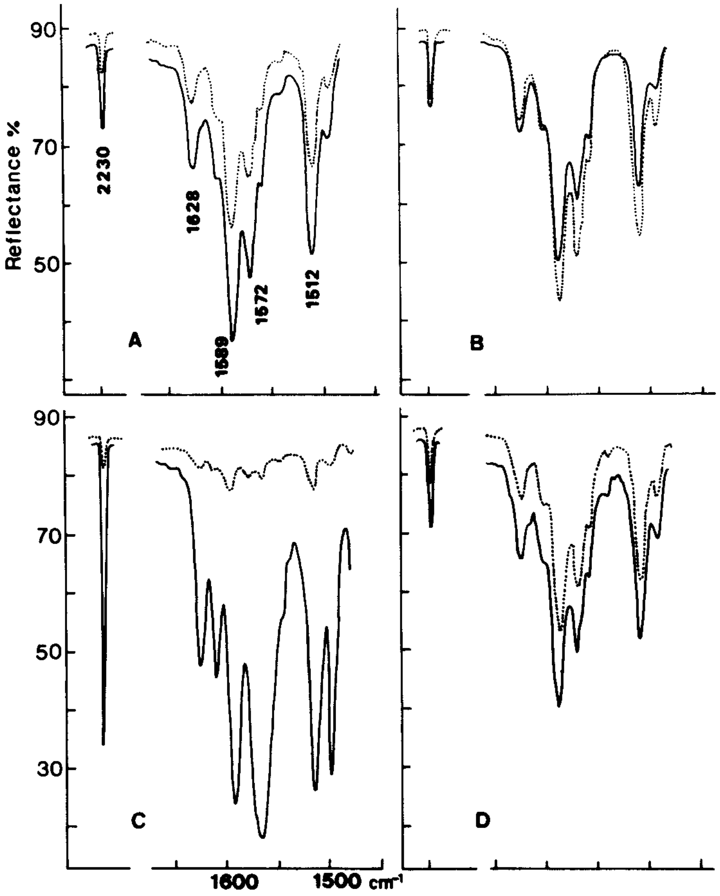

FIGURE 4 Polarized ATR spectra of EBCA between a Si prism and an In_2O_3-coated glass plate. A: isotropic (at 140°C), B: nematic (at 110°C), C: solid (at 100°C), D: nematic (at 110°C) obtained after standing the sample C for 100 hr at 25°C. Solid and dotted lines refer to the parallel and perpendicular polarizations of radiation, respectively.

we have $\beta = 16.8°$ for the C≡N stretching. Unless otherwise noted, this β value will be used as standard in calculations of degree of order.

ATR spectra in the absence of electric field

Figure 4 shows the polarized ATR spectra of EBCA recorded at different temperatures. The sample 15 μm thick was sandwiched between a Si ATR prism and an In_2O_3-coated glass plate. Vibrational assignments are as follows. 2230 and 1628 cm^{-1} bands are respectively C≡N and C≡N stretching, and 1589, 1572, and 1512 cm^{-1} bands are all associated with the phenyl ring stretching.

In discussing our ATR spectra, attention should be paid to the following fact: the penetration depth of evanescent wave responsible for the spectra are equally about 1 μm; consequently the information which will be deduced from these spectra refers to the thin layers having this thickness at the Si prism surface, regardless of the cell thickness.

The magnitude of the dichroic ratios taken from A is of the same order for all vibration bands and is close to the value expected for the isotropic orientation. Below the nematic-isotropic transition temperature the dichroic ratios of the spectra decreased with decreasing temperature. Spectra B were observed at 110°C. The spectra remain unaltered after a few hours. The dichroic ratios changing with different types of vibration suggest that the texture is possibly uniaxial and its optical axis is parallel to the x axis defined in Figure 2. Indeed in the light of previous experiments on PAA[12] and MBBA,[4] the above orientation is certainly due to the flow of nematic molecules which occurs dominantly near the liquid/prism interface. By the use of the D value of 0.74 obtained for the C≡N stretching, the degree of order was obtained to be 0.44. Based on this value, one can estimate β values for the remainder of the vibrational bands measured. Obtained values are as follows: 31.6° (1628 cm^{-1}); 19.6° (1589 cm^{-1}); 8.3° (1572 and 1512 cm^{-1}).

The fact that a flow orientation was observed is an indication that the Si prism surface has no strong aligning force. It must, however, be mentioned that the S value obtained above is much lower than the typical value of 0.62 obtained for MBBA,[4] indicating that the influence of the Si prism surface as well as the In_2O_3 electrode surface cannot be neglected completely.

When lowering temperature a marked change in polarized spectra was observed, which should be attributed to the solidification of nematic liquid. Figure 4 (C) represents the spectra recorded at 100°C. Taking into account the magnitude of the dichroic ratios, it is clear that the molecules crystallized in a uniaxial manner with its optical axis perpendicular to the Si prism surface. The well defined orientation observed above can be elucidated in assuming that the crystal growth was controlled by a temperature gradient provided by a slight temperature difference between the silicon prism and the opposite substrate. Another contributing factor which may be more important is the nucleation at the molecules in contact with the Si surface or In_2O_3 surface.

Subsequent measurements in field-off state were made after exposing the liquid crystal cell to atmospheric conditions for long periods of time. When the temperature was raised above the nematic-isotropic transition point, an isotropic texture appeared. After cooling the isotropic liquid the values of the dichroic ratio obtained were 20 to 25% less than that of a random orientation. The observed spectra at 110°C are shown in Figure 4 (D). Although the exact texture of sample D cannot be known from the dichroic data alone, the most probable is the tilted but not uniform texture.

The orientational change with the elapse of time mentioned above may occur from a variety of causes. Alternation of the substrate surfaces due to the adsorption of the material or some impurities probably account for the quenching of flow. The degradation of the material arising from the hydrolysis may also be a contributing factor.[13]

DC electric field-induced orientation

When a static electric field is applied to the thin liquid crystal the field is expected to produce the molecular orientation. This effect is, however, often restrained by the aligning force of the electrode surfaces. In spite of the importance of this problem, no direct information has been obtained about the liquid crystal structure near the electrodes. Furthermore, even if there is no sufficiently strong interaction between the liquid crystal molecules and the electrode surfaces, the structure of orientation near the electrodes may be different from that in the bulk liquid. In what follows, the structure near the electrode determined from ATR measurements will be mentioned. Measurements are classified into three different types by the opposite electrode used. A Si ATR prism was used without any surface treatment as a probing electrode in all of these measurements.

Case a (In_2O_3-coated glass electrode)

The measurements were started with the less ordered texture mentioned above. The Si prism served as a positive electrode. Polarized ATR spectra under different voltages are shown in Figure 5. The spectra obtained at 2 V are close to spectra C of Figure 4, indicating that the texture remains almost unchanged. However a sharp change in spectra was observed at 3 V, as is seen from Figure 5. To show the spectral change in detail, the dichroic ratios of the observed ATR spectra are plotted versus the external DC field in Figure 6. The dichroic ratios generally increase with increasing voltage, indicating a tendency for the molecules to orient themselves parallel to the field direction. This trend reaches saturation at a field of 4 V, suggesting the completion of a homeotropic structure. The largest *D* value shown by the C≡N stretching band means that the C≡N axis lies most closely to the dipolar axis of the molecule. The same is true for the 1572 cm^{-1} band assigned as one of the phenyl-ring stretching vibrations. On the contrary, the transition moment of the C=N stretching is inclined appreciably from the dipolar axis compared with the C≡N stretching.

On the basis of the dichroic ratios in Figure 6 it is possible to obtain *S* values in the case of uniaxial orientation of molecules around the field direction with complete freedom of rotation about the long axes of the molecules.

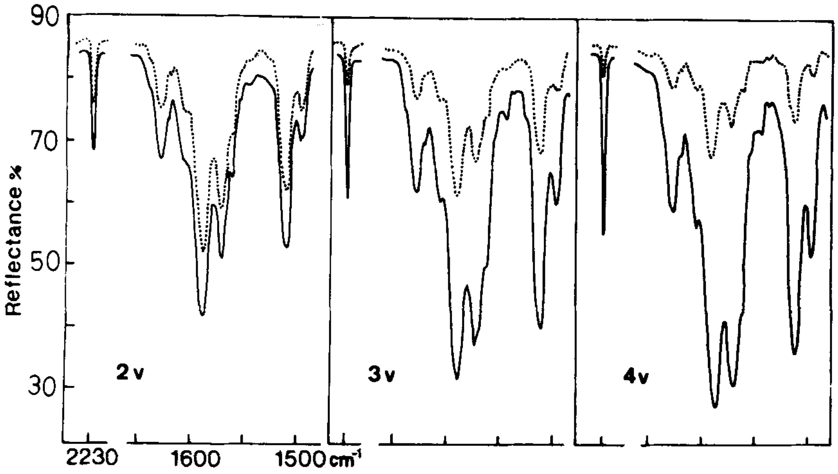

FIGURE 5 Polarized ATR spectra of nematic EBCA at 110°C in a DC electric field; the opposite electrode: an In_2O_3-coated glass plate; the Si prism served as the positive electrode. Solid and dotted lines refer to the parallel and perpendicular polarizations of radiation, respectively.

From the $C\equiv N$ and the $C=N$ stretching bands, the values of S are determined to be 0.59 and 0.61, respectively, by the use of the β values mentioned earlier. From other vibrations at 1589, 1572, and 1512 cm^{-1}, the results are 0.50, 0.53, and 0.50, respectively. As a consequence it may be concluded that the uniaxial model is a good approximation, but the possibility, that the preferred axis deviates a little from the long axis of the molecule, cannot be ruled out.

Figure 7 shows the voltage variation of S as determined from the $C\equiv N$ stretching vibration alone assuming the uniaxial orientation mentioned above. After removal of the DC voltage, a storage effect, in which the texture is not restored to its initial state, was observed. Even after 30 min there remained a homeotropic texture having a degree of order of 0.30. This is not surprising, however, because there is no sufficiently strong nucleation centers directing the molecules parallel to the electrode surfaces. It is supposed that it needs a sufficient time for the domains to fall into decay unless disturbed thermally or electrically.

Indeed, conversion of the persistent texture to the original texture was attained by applying the reverse DC voltage of a definite strength, *i.e.*, when the polarity of the Si prism was changed from positive to negative. This fact indicates that the opposite bias acts as a coercive force in this case. The change of S with the reverse DC voltage is shown by a broken line in Figure 7. Additional field above 4 V produced no significant changes in the texture.

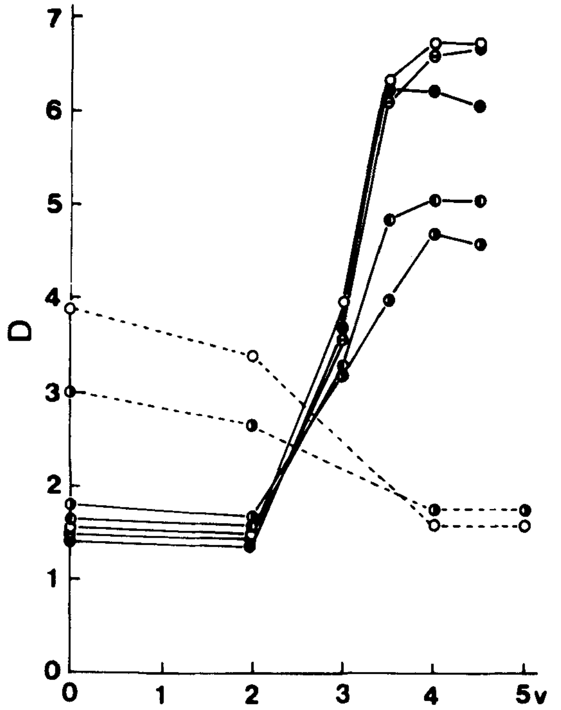

FIGURE 6 ATR dichroic ratio (D) of various vibrational bands as a function of applied DC voltage: ○: 2230, ◑: 1628, ◐: 1589, ⊖: 1572, ●: 1512 cm^{-1}. The Si prism initially served as the positive electrode until the reorientations saturate. After removing the voltage, the reverse DC bias was applied (broken lines).

Case b (Rubbed In_2O_3-coated glass electrode)

To obtain a uniform planar orientation the surface of a clean In_2O_3-coated glass electrode was rubbed with alumina in one direction. The electrode was then positioned to form a cell so that the rubbing direction agrees with the x axis of the Si prism. Nevertheless, the rubbing turned out to be ineffective in producing a tangential alignment. This is presumably a result of strong interaction between the molecules and the In_2O_3 surface which was possibly activated by rubbing. The ATR spectra of the C≡N stretching as a function of applied DC voltage are presented in Figure 8. The magnitude of dichroic ratio in the field-off state may be explained in terms of a less ordered planar alignment in which the long axes of the molecules are oriented at random around the direction perpendicular to the Si surface, but with tilted angles less than 54°44′ which gives $S = 0$.

The values of S calculated from Eq. (2) using $\beta = 16.8°$ for the C≡N stretching were plotted against the externally applied electric field. The

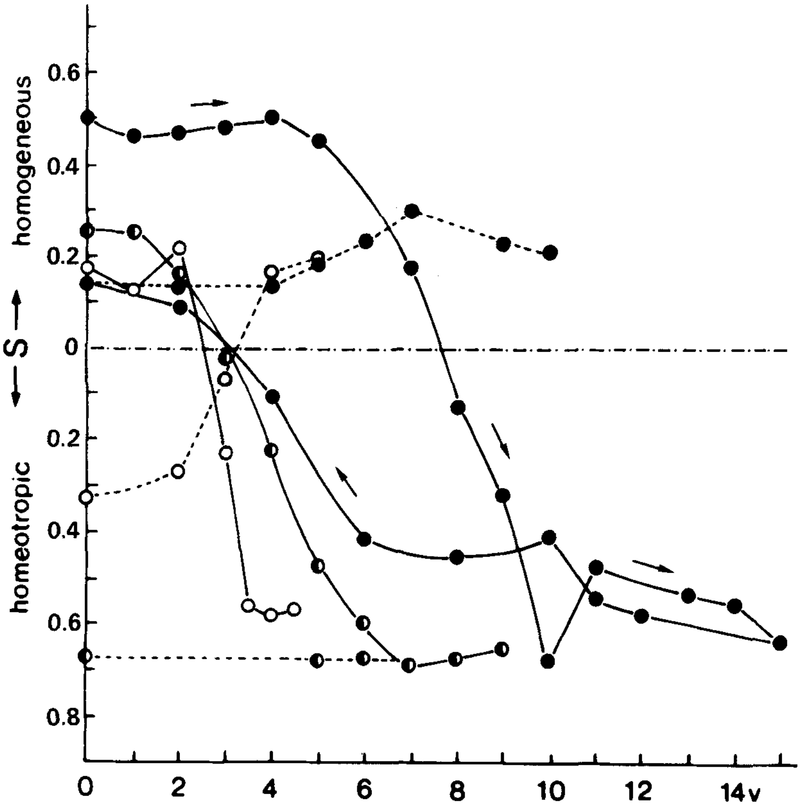

FIGURE 7 Dielectric orientation behaviors of EBCA 1 μm thick in the boundary layers at the Si prism electrode. The opposite electrodes: untreated (○), rubbed (◐), and $C_6H_5SiCl_3$-treated (●) In_2O_3-coated glass plates. Full lines (positive) and broken (negative) refer to the polarity of the Si prism electrode (for details see text).

results are shown in Figure 7. The threshold voltage for the deformation of the original texture is 2 V in agreement with the previous case. However, the change in *S* is not sharp. Moreover, it is very significant to note that once a highly ordered homeotropy was obtained it remained unaltered even if the potential was removed and if the reverse potential was applied subsequently. This effect cannot easily be explained, but it may be related to the bulk liquid structure behind the boundary layers at the Si electrode surface.

Case c (Phenylsilane-coated In_2O_3 glass electrode)

To introduce a planar boundary condition at the opposite electrode, the surface of In_2O_3 glass electrode was treated with $C_6H_5SiCl_3$, following the

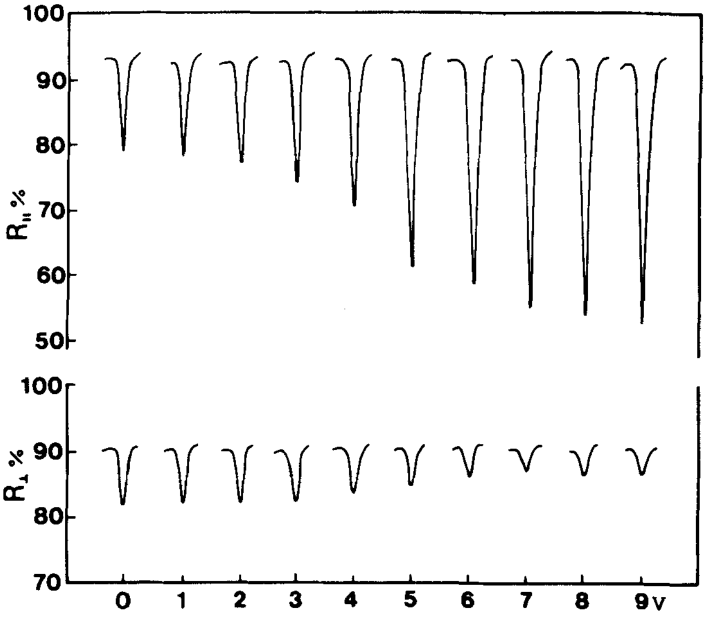

FIGURE 8 Polarized ATR spectra of the C≡N stretching of nematic EBCA at 110°C as a function of applied DC voltage; Si prism served as the positive electrode; the opposite electrode is a rubbed In_2O_3-coated glass plate.

experimental procedure described in the literature.[14] In response to the bulk liquid crystal for which a nonuniform planar alignment may be most favored, the equivalent alignment was expected to be observed near the Si electrode surface. Actually, however, it was a flow alignment with $S = 0.50$. It has already been mentioned that the degree of order of flow alignment was suppressed to some extent by the influence of the Si prism surface. Therefore, it can be considered that the bulk orientation might have displaced the balance of orientation state of the boundary layers at the Si wall surface in favor of an ordered flow. Such the effect must be ascribed to the similarity in the pattern of the flow alignment to the nonuniform planar alignment, because as a general fact no flow orientations have been observed when special procedures to produce a homeotropic texture were followed.[4]

Field effect measurements were made with both increasing and decreasing DC electric fields. The observed changes were not reversible. Figure 7 shows the variation of S of both flow and homeotropic orientations of EBCA as a function of DC electric field. Also in this case, the dichroism of the C≡N stretching was used as a probe of average state of alignment.

S value of the flow texture remains unaltered up to around 5 V. The degree of order of flow decreases rapidly over the threshold voltage about 6 V and disappears completely at 8 V. Comparing with the previous cases the threshold voltage of the orientational deformation is much greater. This is probably because the alignment on the Si electrode is more or less rigid and reorientation competes against liquid crystal elasticity. At higher voltages the director approaches the homeotropic alignment.

As is seen in Figure 7, a sharp hump was observed at 10 V during both increasing and decreasing potential applications. The mechanism of this cause is still unresolved, but the increase of contribution of adjoining bulk orientation may be important. On decreasing DC voltage the degree of order of the homeotropic orientation gradually decreases up to 6 V. Under this voltage the liquid rapidly approaches its random state, in accordance with the larger voltage required for the creation of homeotropic texture. It is noteworthy that the original flow orientation is not restored. After the removal of the field, a reverse DC voltage was applied. Nevertheless, no appreciable effect was observed in the alignment, indicating that the end-over-end motion of dipolar axes and, in turn, of the molecules is severely hindered.

In this study we have confined our interest to the boundary layers 1 μm thick near the Si prism electrode. As we have seen, the molecules in the narrow region were quite well oriented under the influence of DC electric field. However, the threshold voltage for dielectric orientation changed depending upon the opposite electrode used. This means that the detailed structure of bulk liquid which may strongly couple with the boundary layers would play a part in molecular reorientation behaviors. Recently we have carried out similar measurements on EBCA by a transmission technique. The results will be reported in the near future.

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