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Application of Infrared ATR Spectroscopy to Liquid Crystals. IV. A Comparison of Molecular Alignments of Nematic EBCA in Bulk and Boundary Layers under an External DC Electric Field

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Application of Infrared ATR Spectroscopy to Liquid Crystals. IV. A Comparison of Molecular Alignments of Nematic EBCA in Bulk and Boundary Layers under an External DC Electric Field

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Infrared transmission and ATR measurements have been performed on dielectric positive N-(p-ethoxybenzylidene)-p'-cyanoaniline (EBCA) under the combined influences of the weak anchoring and an external DC electric field. The threshold voltage for observing the dielectric molecular orientation was found to be 4 V for a bulk liquid 15 μm thick between Si electrodes. For the molecules in the boundary layer about 0.6 μm thick at the Si electrode, the apparent threshold was 6 V. Differences in the variations of order parameter with voltage were also found between the bulk and boundary layers.

INTRODUCTION

Infrared spectroscopy has been used quite extensively to elucidate liquid-crystal structures at the molecular level. Despite this fact the investigation dealing with the effect of an external electric field (DC or AC) on liquid crystals has been quite limited. Neff, Gulrich, and Brown have measured the infrared dichroism of N-(p-methoxybenzylidene)-p'-cyanoaniline in a DC electric field and have reported a maximum value of 0.33 for the degree of orientational order.[1] The experiments of Ohnishi on MBBA have shown the change in the average direction of the molecular long axes associated with the dynamic scattering.[2] The influence of an AC electric field on the half-widths of infrared absorption bands has been studied for the determination of bending elastic constants of nematic liquid crystals.[3] Flay, Hilsum, and Jones[4] have measured the scattering properties of some field-induced textures and have discussed the possibilities of using liquid crystals as infrared modulators.

However, since all of these studies has employed the conventional transmission method, the measurements have been limited to thin liquid films, typically of 10–50 μm thick. These experiments in principle provide information about average structures, but it is often important to take into account possible interactions between the liquid crystal molecules and the substrate surfaces.[5] Although such interactions have recently become subjects of both basic and applied significance, no spectroscopic measurement in this regard has been carried out. In order to gain a comprehensive understanding of structural properties of liquid crystals, measurements are required on the bulk liquid as well as on the boundary liquid.

Recently, an ATR technique has been introduced as a related method of measuring absorption spectra of liquid crystals.[6–8] One of the most attractive aspects of this technique is that it can provide the three-dimensional information of a liquid crystal in thickness as small as 1 μm or less at the liquid/solid interface under suitable conditions.

The object of the present study is to throw light on the difference in molecular alignment between the bulk and boundary liquid-crystal layers when a DC electric field is applied. The infrared absorption measurements by a combination of transmission and ATR techniques were done on nematic N-(*p*-ethoxybenzylidene)-*p*′-cyanoaniline (EBCA) having a positive dielectric anisotropy.

EXPERIMENTAL

The experimental technique for ATR measurements were similar to those reported earlier.[7] The sample of liquid crystal was sandwiched between a Si ATR prism and a Si plate which served as substrates and electrodes. The infrared beam was incident upon the internally reflecting interface of the Si prism at an angle of incidence of 40°.

In transmission measurements the sample was placed between two Si wafers 0.7 mm thick served as windows and substrates as well as electrodes. The sample was maintained at the required temperatures by an electric heater embedded in mica plates in contact with the Si wafers. In both transmission and ATR measurements, the spacing between the electrodes was adjusted to 15 μm by a polyester film. The liquid crystal sample of EBCA was essentially the same as that described previously.[9] In this study,

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the absorbance of the C≡N stretching vibration at 2230 cm^{-1} was used as a measure of the molecular orientation order in EBCA.[9]

RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra of the C≡N stretching vibration of EBCA 15 μm thick in the nematic phase at 110°C under different strengths of applied DC electric field. The dashed line in Figure 1 represents the spectrum observed at an isotropic temperature of 140°C. It is seen from the figure that in passing from the isotropic to the nematic phase the absorbance (or optical density) decreases significantly. At the same time the background transmittance also diminishes. The former fact shows that there is a certain amount of anisotropy in the liquid, while the latter may be ascribed to the light scattering caused by orientational fluctuations.[10]

Measurements using a polarizer were also carried out, but no significant dichroism was observed though the orientation of the plane of polarization relative to the sample cell was altered. This implies a uniaxial orientation of the molecules around the direction of incoming radiation. Taking into

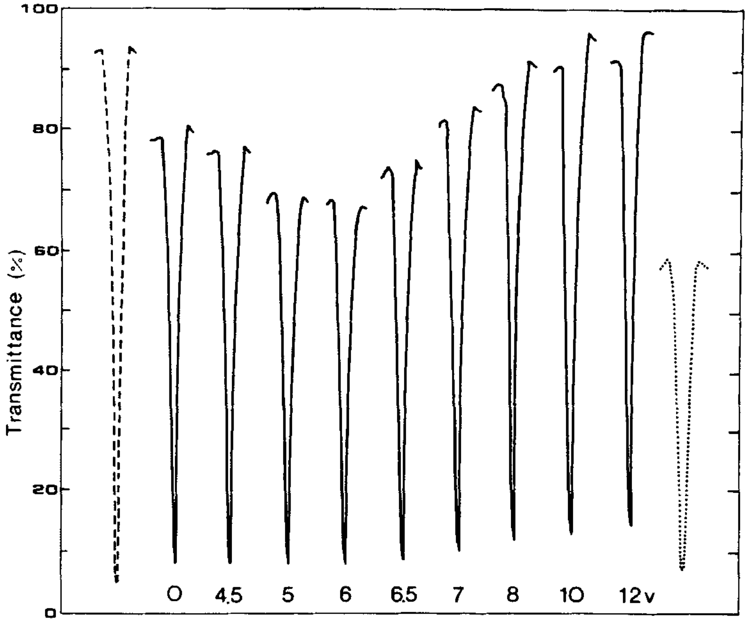

FIGURE 1 Transmission spectra of nematic EBCA (110°C) depending upon applied DC voltage. The dashed line represents the spectrum of isotropic state (140°C). The dotted line indicates the spectrum obtained after switching off a bias voltage of 30 V.

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account that the transition moment of the C≡N stretching makes a small angle with the long axis of the molecule,[9] the diminution in absorbance stems probably from the fact that a large fraction of the molecules in the bulk orients at small angles with the normal to the substrate surfaces. In this case the degree of orientation order which is defined with respect to the average orientation of the long axis of the molecule relative to the optical axis is given by $S = (1 - R)/S_\beta$, where $S_\beta = (3\cos^2\beta - 1)/2$, and β is the angle between the direction of the transition moment and the long axis of the molecule.[11] Furthermore, R is the ratio of the absorbance in the homeotropic phase to that in the isotropic phase. Using the above relation and assuming $\beta = 16.8°$ for the C≡N stretching of EBCA,[9] the S value of the homeotropic orientation reduces to 0.28. The low value thus obtained for the bulk suggests that interactions between the EBCA molecules and Si surfaces are not sufficient to produce a strong birefringent texture even though the orienting influence of Si surfaces is non-negligible.

Figure 2 shows a plot of the resulting S as a function of applied DC voltage. The S value is virtually invariant up to 4 V, but increases gradually with the increase in voltage, reaching a saturation value of 0.44 at 12 V. This confirms the dielectric positive anisotropy of the molecules, but the ordering is rather restrained similarly to the result of Neff *et al.*[1]

As can be seen from Figure 1, the change in degree of orientation order is accompanied by a variation of background transmittance. It begins to decrease approximately at 4.5 V and assumes a minimum value at 6 V. The relative change of the background transmittance is plotted in Figure 2 as a function of the voltage. The above phenomenon is very similar to that reported by Neff *et al.*,[1] and is believed to be caused by the scattering of incident radiation by molecular aggregates or domains induced by the electric field. At voltages above 6 V the background level increases and even passes over the initial value. It reaches saturation at 10 V. It is interesting to note that the decrease in background level begins near the threshold voltage for the dielectric orientation of the molecules in the bulk. Very probably this means that the light scattering mentioned above is closely related to the improvement in homeotropy of the bulk.

The drop in background transmittance was also observed when a sufficiently strong field beyond 6 V was turned off; the higher the applied field, the greater the effect. For example, the dotted line in Figure 1 represents the spectrum obtained after an applied voltage of 30 V was removed. In this case the magnitude of the absorbance demonstrates that the texture apparently reverts to the initial undisturbed state though not completely. The simultaneous decrease in background transmittance may probably be explained in terms of light scattering arising from new discontinuous structures like domain walls in the liquid.

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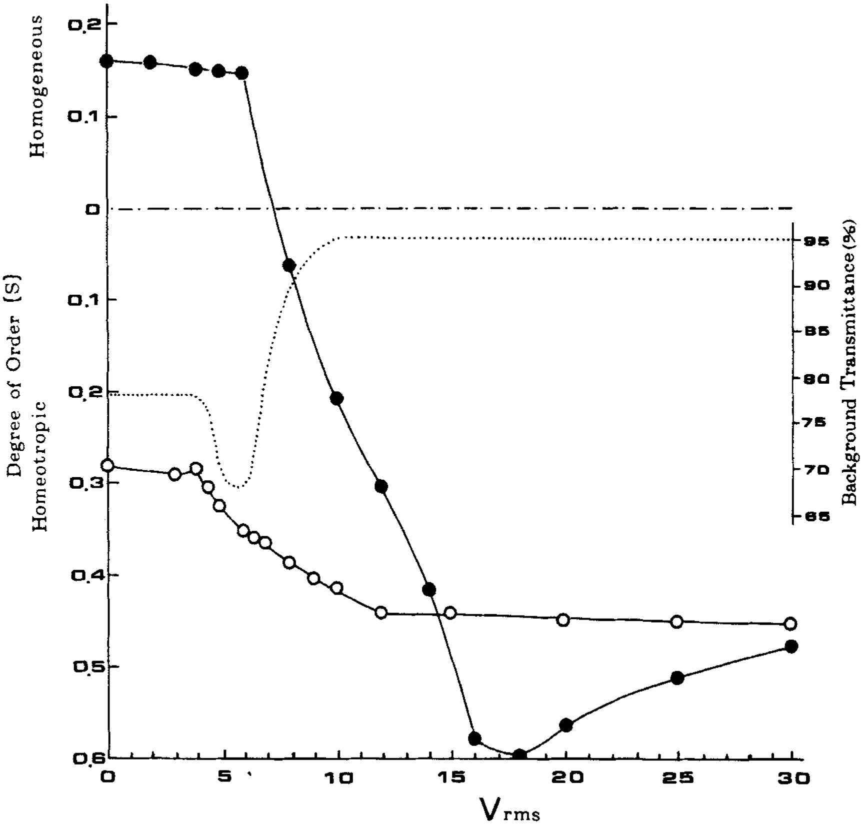

FIGURE 2 Dielectric orientation behaviors of EBCA 15 μm thick between Si electrodes (○) and EBCA 0.6 μm thick at the Si electrode (●). The dotted line shows the change in background transmittance vs applied DC voltage (see Figure 1).

For ATR spectroscopy, the absorption spectrum arises from the interactions of the evanescent wave with the medium near the totally reflecting surface. The absorption intensity is proportional to the penetration depth of the evanescent wave which takes on a wide range of value depending on the refractive index of reflecting prism, the angle of incidence, and the wavelength of radiation. In our experimental conditions, the effective penetration depth is estimated to be ca. 0.6 μm.[12]

Figure 3 shows the polarized ATR spectra of the C≡N stretching of nematic EBCA at 110°C as a function of applied DC voltage. The upper and lower spectra were measured with the radiation polarized parallel and perpendicular, respectively, to the plane of incidence. Mention has already been made of the method of determining orientations based on dichroism.[7]

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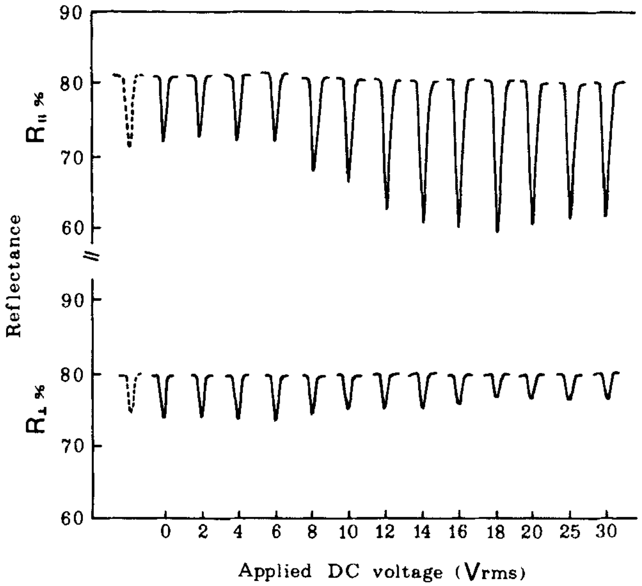

FIGURE 3 Polarized ATR spectra of nematic EBCA (110°C) as a function of applied DC electric field. The Si prism served as a positive electrode. Upper and lower spectra were measured with the radiation polarized parallel and perpendicular to the plane of incidence, respectively. The dashed lines represent the spectra of isotropic phase at 140°C.

The magnitude of the dichroic ratio in field-off state shows that the molecules at the boundary are neither homeotropic nor random; possibly two orientations can be considered, one with the preferred axis directed perpendicular to the plane of incidence (viz., homogeneous) and one with that axis tilted. Although the orientation cannot be determined uniquely at present, the difference in orientation profile between the bulk and boundary liquids was revealed for the first time.

The origin of the above result is difficult to account for, because the mechanism of liquid crystal growth in weak anchoring conditions would be expected to be more delicate in general than that in strong anchoring conditions. Experimental evidence indicates, however, that nematic liquid crystal molecules at the boundary do flow along vertical cell walls unless there are strong interactions between the molecules and wall surfaces.[8,9] Judging from the non-uniformity of the bulk as already mentioned, it is likely that the flow would react to some extent on the boundary orientation which most probably is homeotropic. If this picture is correct, the result is to produce homogeneous domains or tilt domains at the boundary, while far from the walls a homeotropic alignment is substantially retained as observed.

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Assuming a uniaxial alignment of the long axes of the molecules about the field direction, the value of degree of orientational order was calculated. The results are shown in Figure 2. The threshold voltage for the dielectric orientation is 6 V, a value which is larger than that obtained for the bulk. One notices that light scattering observed in transmission experiments was a maximum at this voltage. This fact strongly suggests that marked difference in orientation profile between the bulk and boundary liquids is the dominant mechanism giving rise to the light scattering. Furthermore, the scattering centres are probably formed between the bulk and boundary regions.

Above 6 V, *S* value steeply increases and reaches a maximum at 18 V. The decrease in scattered light associated with orientation ordering of the boundary and in turn the formation of uniform homeotropy throughout the entire liquid agree well with the scattering-centre formation. It must, however, be pointed out that for strong fields above 18 V the degree of orientational order decreases, approaching to that of the bulk.

CONCLUSIONS

A comparison has been made between the bulk and boundary liquids of nematic EBCA molecules with respect to the orientational behaviour in a static electric field under relatively weak anchoring conditions. The effect of the DC field was essentially to produce a homeotropic texture in either region. Values of the threshold voltage different from each other were obtained for the bulk and boundary liquids, the one for the former being lower. Nevertheless, higher degrees of orientation order were attained for the boundary liquid at relatively strong fields, confirming the existence of different effective fields in different regions of the film.

As we have seen, the polarized ATR technique is considerably more sensitive to the orientational behavior of the surface region than the bulk. In the present study, ATR measurements were all made at a fixed-angle of incidence because of the limited flexibility of the ATR optics used. Obviously, an improved way of developing the present ATR approach is to use the variable-angle method.[13] If ATR spectra are measured as a function of angle of incidence, orientation information may be obtained as a function of distance from solid/liquid interface and so this technique may be useful for interpreting a number of phenomena in liquid crystals where surface effects are important.

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