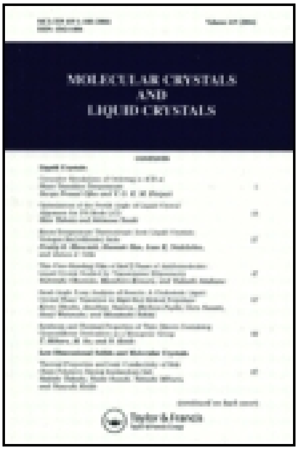

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Anomalous Alignment and Dynamic Scattering in Liquid Crystals Exhibiting a Positive Dielectric Anisotropy†‡

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Abstract—Molecular alignment owing to ionic conductivity anisotropy, Williams' Domains and dynamic scattering have been observed in the nematic phase of *p*-butyloxybenzoic acid which exhibits positive dielectric and conductivity anisotropies. This was observed for both dc and ac electric fields. Other nematic materials with positive dielectric anisotropies which do not show strong ac effects are discussed. The possibility of hydrogen bonds breaking at the transition temperature to account for a change in the microwave dielectric loss is mentioned.

1. Introduction

The effects of electric fields on the molecular alignment in nematic materials exhibiting a negative dielectric and positive conductivity anisotropy have been studied extensively. For resistivities of the order of 10^9 ohm-cm or less in these materials, the long molecular axes usually prefer a direction perpendicular to an electric field for frequencies above the audio region, and parallel to the field for dc and very low audio frequencies. It is believed(1) that this effect is associated with the counteraction of dielectric and conductivity anisotropy which are of opposite sign, and the space charge relaxation time which results from the conductivity anisotropy. Domains(2) owing to very low frequency electric fields have been satisfactorily explained(3,4,5) using this idea. Felici(6) has presented a

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theory for domains owing to dc electric fields, but the behavior in a dc field is not as well understood.

An anomalous effect in the smectic *A* phase of ethyl-*p*-[(*p*-methoxybenzylidene)]amino cinnamate (EMC) has been observed.⁽⁷⁾ In the nematic phase of this material the preferred direction for the long molecular axes was parallel to an electric field for both dc and high audio frequency fields. This phase exhibits a positive dielectric anisotropy. As the sample was cooled into the smectic phase in the presence of external electric fields, the preferred direction for the long molecular axes was parallel to the field for frequencies of a few thousand Hz and perpendicular to a dc field. Since the conductivity in the smectic phase was found to be greatest perpendicular to the long molecular axes, a mechanism comparable to that suggested earlier⁽¹⁾ to explain the anomalous effects in nematic materials was proposed.

The nematic phase of 4,4′ di-*n*-heptyloxyazoxybenzene (HOAB) exhibits a negative dielectric anisotropy⁽⁸⁾ and a negative conductivity anisotropy.⁽⁹,¹⁰⁾ A 25 Hz electric field was found⁽⁹⁾ to be more effective than a 5000 Hz field in ordering the molecules with the long axes preferring a direction perpendicular to the electric field. This was accomplished by changing the direction preferred by the long molecular axes in a magnetic field with the aid of electric fields. De Vries⁽¹¹⁾ has suggested that HOAB has a cybotactic structure in its nematic phase, i.e., the long axes of the molecules are at approximately 45 degrees to planes which intersect the center of the axes of the molecules. Chistyakov and Chaikowski⁽¹²⁾ have also investigated the nematic phase of HOAB and reported a more acute angle between the direction preferred by the long molecular axes and the planes. It could be assumed, as was done for the smectic *A* phase, that charges flow more easily along the boundary layers of the cybotactic groups than in any other direction and this could account for the observed conductivity anisotropy. This work is consistent with other work on nematic and smectic phases in that the aligning mechanism, which is believed to be associated with the conductivity anisotropy, favors an ordering such that the direction of maximum conductivity is parallel to the electric field. Therefore, a mechanism similar to that proposed earlier for nematic⁽¹⁾ and smectic phases⁽⁷⁾ was suggested.

Some work(13,14) has been carried out involving molecular alignment owing to electric fields in nematic materials which exhibit a positive dielectric anisotropy. A 60 Hz electric field was slightly more effective(13) than a 370 kHz field in a decomposed sample of anisal-*p*-aminoazobenzene. In the nematic phase of ethyl-*p*-[(*p*-methoxybenzylidene)amino] cinnamate(14) (EMC) the difference between the results for a dc and a 5000 Hz electric field may be due to turbulence created by the dc field. Results for frequencies much greater than 5000 Hz in EMC were comparable to those employing a 5000 Hz electric field. In the work reported here we show that the effectiveness of electric fields in producing molecular alignment is strongly dependent on the frequency of the applied field for *p*-butyloxybenzoic acid which has a positive dielectric anisotropy.

The general position of the literature in relation to dynamic scattering(15) (discussed first for nematics with negative dielectric anisotropy) in nematics exhibiting a positive dielectric anisotropy is a little confusing. Statements have been made which imply that a nematic material should have a negative dielectric anisotropy if they are to exhibit dynamic scattering in an electric field. Elliott and Gibson(16) observed domains in anisal-*p*-aminoazobenzene and reported that it scattered light in a dc field. Kapustin, Trofimov and Chuvyrev(17) reported similar results for *p*-butyloxybenzoic acid. A nucleated weak turbulence has been observed by Rafuse and Soref(18) in carbonate schiff bases in ac fields below 100 Hz. Gruler and Meier(19) reported finding Williams' Domains in 4,4′ di-*n*-heptyloxyazobenzene that show a frequency dependence for the threshold voltage, but they did not report light scattering above the threshold voltage. Durand and Pontikis(20) and also de Jeu(21) have observed a frequency dependence for a threshold voltage for domains in a nematic material with a positive dielectric anisotropy. They observed interesting effects above the voltage threshold but are reluctant to call it dynamic scattering. In this article the authors are reporting what is believed to be dynamic scattering in a nematic phase, exhibiting a positive dielectric anisotropy, employing ac electric fields.

2. Experimental

The microwave techniques employed in this work were similar to those reported earlier.(13) For domains and dynamic scattering measurements a typical sandwich cell(2) was used. The samples of *p*-butyloxybenzoic acid (BOBA) were obtained commercially. They were first purified by recrystallization then further purified by zone refining. The dc resistivity was 10^8–10^9 ohm-cm.

3. Discussion

A. DIELECTRIC MEASUREMENTS

Figure 1 shows the temperature dependence of the dielectric loss for *p*-butyloxybenzoic acid at a frequency of 24 GHz. The upper and lower curves show the dielectric loss in the presence of a magnetic field with the symmetry axis of the sample aligned perpendicular and parallel to the polarized microwave field, respectively. If the mechanisms responsible for the absorption at the two orientations are the same, the average absorption in the nematic phase is

$$\epsilon'' = \tfrac{1}{3}(\epsilon_{\parallel}'' + 2\epsilon_{\perp}''),$$

where $\epsilon_{\parallel}''$ and $\epsilon_{\perp}''$ represent the dielectric loss for the external magnetic field applied parallel and perpendicular to the microwave field, respectively.

Figure 1 shows the average value of the dielectric loss changes abruptly at the nematic–isotropic transition temperature. A change of this magnitude has not been observed at the nematic–isotropic transition temperature for liquid crystals investigated previously. A possible explanation is that the characteristic relaxation time which is associated with the microwave absorption is much shorter in the normal liquid just above the transition temperature than in the nematic phase. Axmann(22) has measured the characteristic relaxation time in 4,4′-di-*n*-hexyloxyazobenzene and 4,4′-di-*n*-octylazobenzene and reported no appreciable changes in the relaxation times at the transition temperature. Since the *p*-*n*-alkoxybenzoic acids are believed to form linear dimers(23) then dielectric properties should be similar to the 4,4′-di-*n*-alkoxyazobenzenes, with the alkoxy groups being primarily responsible for the dipole moments. In view of Axmann's results, it seems unlikely that a change in the relaxation time would be entirely responsible for the change in the dielectric loss at the transition temperature. An idea which was

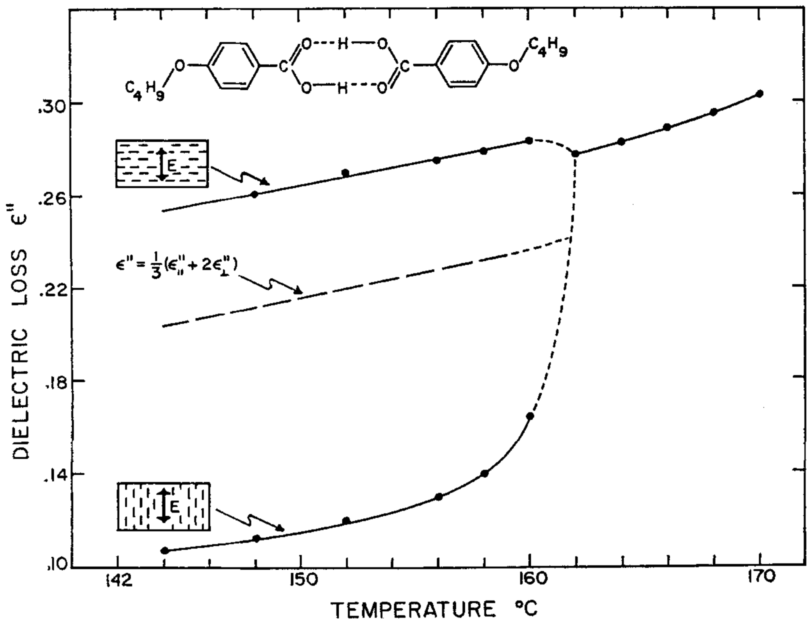

Figure 1. Temperature dependence of the dielectric loss at a frequency of 24 GHz in a magnetic field of 4000 G parallel and perpendicular to the microwave electric field for *p*-butyloxybenzoic acid.

discussed earlier[24] assumes that BOBA is not 100% dimer but contains a small percentage of monomer. The possibility of only one of the hydrogen bonds breaking in the dimer must also be considered. If the percentage of monomer or dimer with one broken bond changes abruptly (small change) at the nematic–isotropic transition the change in dielectric loss could be accounted for. Schulz and Meier[25] have made low frequency dielectric measurements in BOBA and found some unusual behavior. Work by Deloche and Cabane[26] also supports the idea that in the nematic phase we do not have 100% dimer with both hydrogen bonds. They have investigated the coupling of hydrogen bonding to orientational fluctuation modes in a liquid crystal.

In an earlier article it was reported by one of the authors (EC) that the dielectric anisotropy in *p*-heptyloxybenzoic acid appeared to change sign at nematic–smectic *C* transition. This has been rechecked and found to be incorrect. Alignment studies employing electric fields indicate that it exhibits a negative dielectric anisotropy in both phases. This seems a little unusual since BOBA exhibits a positive dielectric anisotropy. The dielectric anisotropy is very small in each case so we cannot take it very seriously, but the breaking of only one of the hydrogen bonds in *p*-heptyloxybenzoic acid might account for the anisotropy. Preliminary measurements in *p*-heptyloxybenzoic acid also indicate a change in the dielectric loss at the nematic–isotropic transition.

B. Electric Field Effects

Figure 2 illustrates the effect of an electric field on the molecular alignment in BOBA at a temperature of 152 °C. The symmetry axis of the sample was initially aligned perpendicular to the microwave field by a 2000 G magnetic field, thus giving maximum absorption. As the external electric field was increased, a value of the field was reached such that the symmetry axis was rotated 90 degrees. The results shown in Fig. 2 indicate that the electric fields of lowest

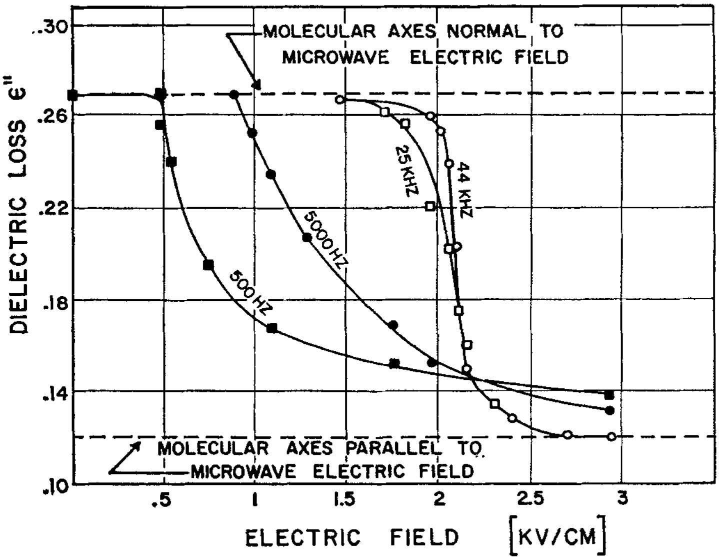

Figure 2. Dielectric loss for *p*-butyloxybenzoic acid at a frequency of 24 GHz as a function of an externally applied ac electric field. The individual curves are for various frequencies of the externally applied electric field. A magnetic field of 2000 G was applied perpendicular to the microwave and externally applied electric fields and the temperature was 152 °C.

frequency are most effective in changing the direction of the symmetry axis. Increasing the frequency above 44 kHz did not produce any appreciable changes, so it is quite certain that BOBA exhibits a positive dielectric anisotropy. Schulz and Meier(25) also agree that the dielectric anisotropy is positive. It is believed that the realignment in the 44 kHz electric field involves only the dielectric properties, but at much lower frequencies the rotation of the symmetry axis is aided by a mechanism associated with the ionic conductivity anisotropy. This is very likely the same mechanism(1) which is responsible for the anomalous alignment in nematics exhibiting a negative dielectric anisotropy. In this case the space charge resulting from the conductivity anisotropy can interact with the electric field and produce a rotation that is in the same direction as that produced by the mechanism associated with the dielectric anisotropy.

The range of field strengths necessary to produce a rotation of the symmetry axis is much greater for the lower frequencies. This was also the case for anomalous effects in nematics with a negative dielectric anisotropy.

The results in Fig. 3 are similar to those in Fig. 2 except measurements were made using magnetic field strengths of 2000 and 4000 G instead of only one value of the field. The curves for the 44 kHz field are equally spaced which is to be expected from a dielectric effect. The curves for the 500 Hz field also appear to be evenly spaced (other data with many different values of the magnetic field agreed with this observation). This is consistent with anomalous effects(1) in nematics with a negative dielectric anisotropy for magnetic fields in the range 2000–10,000 G. However, it should be noted that the low frequency curves are not as evenly spaced as those associated with the dielectric mechanism.

BOBA did exhibit Williams' Domains in both dc and ac electric fields. The frequency dependence for the threshold voltage for domain formation was very similar to that reported by Gruler and Meier(19) for 4,4′-di-*n*-heptyloxyazobenzene, except the cut-off frequency was much higher for the Williams' Domains. Above the threshold voltage and below the cut-off frequency, intensive light scattering was observed in BOBA which appeared comparable to the dynamic scattering observed in *p*-azoxyanisole. The authors are not aware of any work in nematics, exhibiting a positive di-

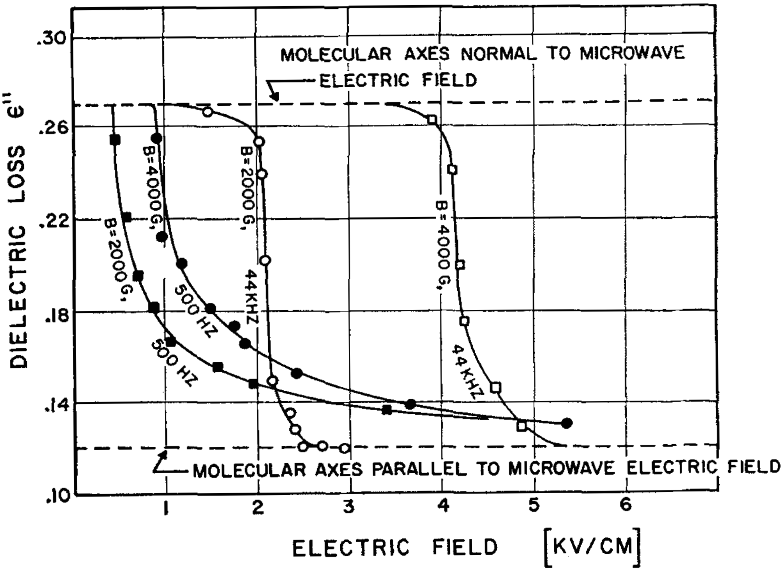

Figure 3. Dielectric loss for *p*-butyloxybenzoic acid at a frequency of 24 GHz as a function of an externally applied ac electric field. Magnetic fields of 2000 and 4000 G were applied perpendicular to the microwave and externally applied electric fields. The frequencies for the externally applied electric fields were 500 Hz and 44 kHz and the temperature was 152 °C.

electric anisotropy, which shows dynamic scattering comparable to that observed in *p*-azoxyanisole in ac fields. Rondelez$^{(10)}$ has observed dynamic scattering in *p*-octyloxybenzoic acid but this material may exhibit a negative dielectric anisotropy. BOBA is the only material investigated thus far with a positive dielectric anisotropy, which shows strong ac effects in the bulk sample owing to the ionic conductivity anisotropy. Therefore, there may be a close connection between ionic conduction induced alignment in the bulk sample and dynamic scattering. Recent work$^{(27)}$ at the Phillips Research Laboratories indicates that very pure nematics with a positive dielectric anisotropy do not show Williams' Domains. This supports the idea that some ionic impurity is necessary for domains, dynamic scattering and an electric field effect at very low frequencies in BOBA.

An attempt to observe domains and light scattering in anisal-*p*-aminoazobenzene showed domains and scattering in a dc field which agreed with Elliott and Gibson,(1) but only transient and nucleated weak turbulence was observed in ac electric fields. This could be expected since the mechanism associated with the conductivity anisotropy(13) appears to have only a slight effect on the molecular alignment in the bulk sample. Preliminary measurements have indicated that anisal-*p*-aminoazobenzene has a positive dielectric and conductivity anisotropy. The percentage and type of impurity may be quite critical for ionic conduction induced alignment in this material, and the impurity in a used sample is probably not uniformly mixed. This might allow certain small regions within the bulk sample to be critically mixed and be responsible for the results obtained.(13) The nucleated weak turbulence which is often observed in the typical sandwich cell might also be due to certain regions that become critically mixed.

4. Conclusion

Molecular alignment owing to ionic conductivity anisotropy, Williams' Domains, and dynamic scattering have been observed in a nematic phase with positive dielectric and conductivity anisotropies. This was observed for both dc and ac fields. Although there may be some confusion in the literature concerning materials with a positive dielectric anisotropy, there does not appear to be any disagreement between these observations and the work of Penz(28) who has extended the work by Helfrich.(3)

The results for BOBA imply that there is a close connection between dynamic scattering and molecular alignment owing to the ionic conductivity, but it is difficult to understand why many other nematic materials with positive dielectric and conductivity anisotropies do not show such strong low frequency effects. The behavior of BOBA is not typical of dimers because *p*-methoxycinnamic acid forms a linear dimer, but fails to show strong low frequency effects. In methoxycinnamic acid the domains were parallel to the direction of rubbing in a dc field rather than perpendicular which is normally observed.

If recent observations(29) are included, molecular alignment owing to ionic conductivity has been observed in nematic phases exhibiting positive dielectric and negative conductivity anisotropies(29) (*p*-

nonyloxybenzoic acid), negative dielectric and negative conductivity anisotropies,⁽⁹⁾ negative dielectric and positive conductivity anisotropies⁽¹·³⁰⁾ and positive dielectric and positive conductivity anisotropies. In all cases an ordering is preferred such that the direction for maximum conductivity is parallel to the electric field. All four cases are consistent with the idea that the alignment is due to an interaction of the electric field with space charge which results from the conductivity anisotropy.

Work reported here and also work by Schulz and Meier⁽²⁵⁾ indicate that the *p*-*n*-alkoxybenzoic acids may exhibit some very interesting dielectric behavior. The possibility of breaking hydrogen bonds at the transition temperature should probably be checked by other methods such as infrared techniques.

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