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Ordering in the Smectic Phase Owing to Electric Fields†‡

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Abstract—A recent article contained results which showed that in the smectic phase of ethyl-[*p*-(*p*-methoxybenzylidene)amino] cinnamate, the molecules preferred a direction with the long axes parallel to a 5000 Hz electric field and perpendicular to a dc field. It was suggested that the anomalous effect in the dc field might be associated with the conductivity anisotropy, since the conductivity was greatest in a direction perpendicular to the long axes of the molecules in the smectic phase. Results are presented which show how the ordering varies with the frequency of the applied field for frequencies below 5000 Hz in the smectic phase of ethyl-[*p*-(*p*-methoxybenzylidene)amino] cinnamate. The ordering in the nematic phase of this material owing to dc and ac electric fields is also described. A few comments are made concerning the nematic and smectic phases of *p*-heptyloxybenzoic acid.

1. Introduction

It was recently reported[1] that the smectic-A phase of ethyl-*p*-[*p*-(methoxybenzylidene)amino] cinnamate (hereafter referred to as EMC) exhibited an anomalous alignment when cooled from the nematic phase in the presence of a dc electric field. The preferred direction for the long axes of the molecules was parallel to the field in the nematic and perpendicular in the smectic phase. For a 5000-Hz electric field the preferred direction for the long molecular axes was parallel to the field in both the nematic and smectic phases. This implies that the low frequency dielectric constant is a maximum in a direction parallel to the long axes of the molecules in both phases,

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and that the ordering in the smectic phase owing to a dc field is an anomalous effect.

The conductivity in the smectic phase is EMC a maximum[1] in a direction perpendicular to the long axes of the molecules and it was suggested that the anomalous effect was associated with the conductivity anisotropy. Because of the low conductivity of the material the conductivity anisotropy was investigated employing a low dc electric field for the conductivity measurements and a high magnetic field for orientating the molecules. Polarization effects make it difficult to know exactly what one is measuring when employing dc fields, but Carr[2] has reported earlier that in the smectic phase of ethylpazoxybenzoate the conductivity was found to be a maximum in a direction perpendicular to the long molecular axes employing an ac field.

In many respects the anomalous behavior in the smectic phase of EMC is similar to that found in the nematic phases of *p*-azoxyanisole[3,4] and *p*-(anisalamino)-phenyl acetate.[5] In these nematic materials the conductivity was a maximum parallel to the long molecular axes rather than perpendicular as observed for the smectic phase of EMC, and the low frequency dielectric constant was a maximum perpendicular to the long axes. This anomalous effect in the nematic materials was attributed[3,6] to the counteraction of dielectric and conductivity anisotropy. Helfrich[7] has presented a theoretical treatment of conductivity induced alignment and two recent articles by the Orsay Group[8] and Penz[9] contain results which give support to this work.

Since earlier work[1] involved only dc and 5000 Hz electric fields, the results reported here will include the effects owing to electric fields at frequencies below 5000 Hz in the smectic phase of EMC. Results showing the effect of ac and dc electric fields in the nematic phase will also be presented. The primary object of presenting the results for the nematic phase is to show that the behavior in the nematic phase of this material is not unexpected rather than to discuss an investigation of the nematic phase. Ordering in the nematic phase of materials exhibiting positive dielectric anisotropy at low frequencies (dielectric constant greatest in a direction parallel to the long axes of the molecules) is more involved then indicated in this work and will be discussed later. Vorlander[10] reported one nematic and two smectic phases for EMC and these were later

discussed by Demus and Sackmann.[11] The clearing point was reported to be 138.5 and the nematic to smectic-A transition point was given as 117.6 °C.

Preliminary measurements were made with *p*-heptyloxy benzoic acid which exhibits a nematic and a smectic C phase,[12] and a few comments will be made concerning this material.

2. Experimental

The experimental techniques employed in this work were similar to those reported earlier.[6] This method uses measurements of the dielectric loss at a microwave frequency of 24.5 GHz to determine the degree of alignment. Since the amount of power transmitted through a sample depends on the orientation of the molecules, measurement of the absorption can provide information about the ordering of the molecules.

Earlier work[13] showed that the absorption (dielectric loss) was a maximum when the long axes of the molecules were aligned perpendicular to the microwave electric field and a minimum for a parallel alignment. Since the external electric field is always applied parallel to the microwave electric field, large values for the dielectric loss imply that the long molecular axes prefer a direction perpendicular to the electric field and low values imply that the preferred direction is parallel to the field. The intensity of the microwave field was too low to have any effect on the ordering of the molecules.

EMC was obtained commercially and purified by recrystallization from ethanol. *P*-Heptyloxybenzoic acid was also obtained commercially and purified by recrystallization.

3. Results and Discussion

A. Smectic Phase of EMC

The results shown in Fig. 1 illustrate the effects owing to low frequency electric fields in EMC. All measurements were made as the sample was cooled slowly from the nematic to the smectic phase in the presence of external fields. The upper dotted line[1] shows the dielectric loss as the sample was cooled in the presence of a 10,000 gauss magnetic field applied perpendicular to the microwave

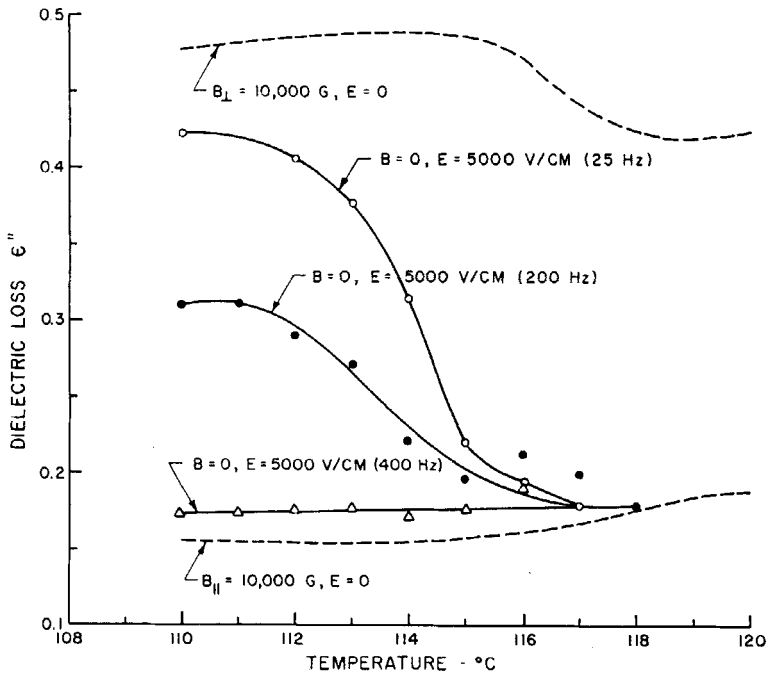

Figure 1. Dielectric loss in EMC at a microwave frequency of 24.5 GHz as a function of temperature. A magnetic field of 10,000 G was applied parallel and perpendicular to the microwave electric field (dotted lines). 5000 V/cm electric fields at frequencies of 25, 200 and 400 Hz are applied parallel to the microwave field.

electric field. The increase in loss in the neighborhood of the nematic–smectic A transition point is believed to be due to an increase in the degree of order in EMC. The lower dotted line[1] shows the dielectric loss as the sample is cooled in the presence of a 10,000 gauss magnetic field applied parallel to the microwave electric field. The absence of a significant drop in the loss near the transition point is believed to be due to wall effects. The walls of the container produce an ordering with the long axes of the molecules favoring a direction parallel to the walls of the container.

When the sample is cooled in the presence of a 25 Hz electric field (5000 V/cm), there is a large increase in the dielectric loss as we enter the smectic phase, as is indicated in Fig. 1. This implies an ordering with the long molecular axes preferring a direction parallel to the electric field in the nematic and perpendicular to the field in the

smectic phase. These results are comparable to those reported earlier which employed a dc field. For a 200 Hz electric field (5000 V/cm) the preferred direction for the long molecular axes in the smectic phase is difficult to determine, but at 400 Hz the long axes prefer a direction parallel to the field in both phases. For fields of much higher frequency the loss is comparable to that with a 10,000 gauss field applied parallel to the microwave field. The critical frequency region (region above which the anomalous effect is not observed) was found to be very sensitive to impurity. Measurements were made the following day on the sample used to obtain results shown in Fig. 1, and the dielectric loss in the presence of a 500 Hz electric field was found to be comparable to that shown in Fig. 1 for a 200 Hz field.

Since the molecules prefer a direction with their long axes parallel to an electric field in both the nematic and smectic phases for frequencies of a few thousand cycles and higher, these results imply that the low frequency dielectric constant is a maximum in a direction parallel to the long axes for both phases. An ordering with the long axes preferring a direction parallel to the field in the nematic and perpendicular in the smectic phase implies that the ordering in the smectic phase is an anomalous effect.

When a smectic material is ordered by external fields comparable to those used in this work it is often thought that the ordering takes place near the transition point while cooling. The results show that some of the material is ordered while in the smectic phase. This process is slow and the sample should be cooled at a rate of about 5 degrees per minute. As the sample decomposes the response time can change considerably. Occasionally the sample decomposed to the point where only a few seconds were required for the field to produce changes in alignment in the smectic phase.

A very crude model that might help to illustrate an effect owing to the conductivity anisotropy is shown in Fig. 2. If clusters of molecules are arranged as indicated in Fig. 2a, space charge should accumulate due to the externally applied electric field. This assumes that the conductivity is a maximum in a direction perpendicular to the long molecular axes. If one could arrange clusters of molecules as shown in Fig. 2b and use the idea illustrated in Fig. 2a, space charge should accumulate as illustrated. This space charge could

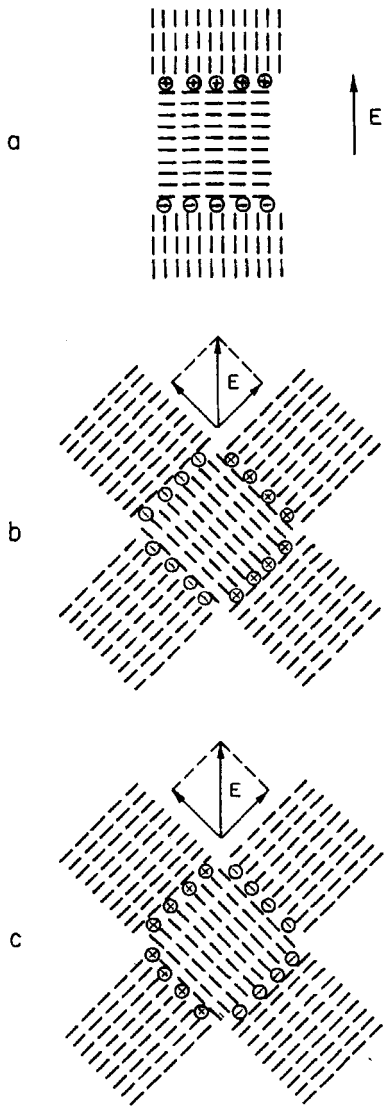

Figure 2. Model to illustrate interfacial polarization in smectic liquids exhibiting a positive dielectric anisotropy. (a) and (b) conductivity anisotropy, (c) dielectric anisotropy.

interact with the external field. If the dielectric constant is a maximum in a direction parallel to the long molecular axes, the boundaries would appear charged as illustrated in Fig. 2c owing to the low frequency dielectric anisotropy. Figure 2c shows that space charge of the opposite sign appears at the boundaries when considering dielectric anisotropy rather than the conductivity anisotropy. When ordering occurs there must be movement that is not illustrated in this figure, but the purpose of this diagram is only to illustrate that the conductivity anisotropy and the dielectric anisotropy can be responsible for competing processes.

B. Nematic Phase of EMC

Figure 3 shows the effects of dc and 5000 Hz electric fields on the molecular alignment in the nematic phase of EMC at 125 °C. Since the dielectric loss indicated by the upper dotted line corresponds to an ordering with the long axes of the molecules perpendicular to the

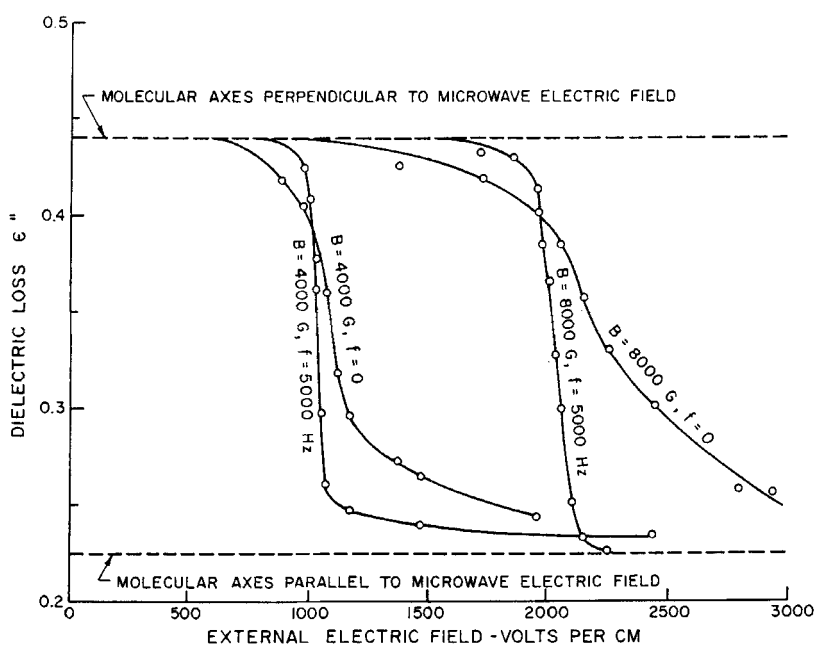

Figure 3. Dielectric loss (24.5 GHz) in nematic phase of EMC at $T = 125°$ as a function of an externally applied electric field. dc and 5000 Hz electric fields were applied perpendicular to 4000 and 8000 G magnetic fields.

microwave electric field and the loss indicated by the lower dotted line is for the long axes parallel to the microwave field, a change in the dielectric loss from the value shown by one of the dotted lines to the value shown by the other corresponds to a 90° rotation of the molecules.

In order to compare the effectiveness of electric and magnetic fields for producing molecular alignment, the electric field was applied perpendicular to the magnetic field because the long axes of the molecules prefer a direction parallel to both fields. With the magnetic field set at 4000 or 8000 gauss, measurements of the dielectric loss were made as the electric field was increased. At a frequency of 5000 Hz the breaks in the curve are quite sharp and equally spaced. This implies that the processes primarily responsible for the ordering involve only the dielectric and diamagnetic anisotropies. Results employing ac fields of a few hundred kHz and also fields at frequencies much below 5000 Hz were comparable to those shown for the 5000 Hz field. The effectiveness of ac electric fields relative to magnetic fields was found to be independent of temperature. The results showing the effect owing to a dc electric field do not show the sharp breaks. It is possible that disturbances created by the dc field may cause some disordering at lower field strengths, but polarization makes the dc field less effective at higher fields.

Figure 3 shows that the behavior of EMC in the nematic phase is not unexpected. However, it should be pointed out that although there are other nematic materials with a positive low frequency dielectric anisotropy that show a similar behavior, butoxybenzoic acid[14] behaves differently at low audio frequencies. In this material fields at low audio frequencies are more effective than fields at much higher frequencies.

C. P-Heptyloxybenzoic Acid

A few preliminary measurements were made on *p*-heptyloxybenzoic acid which exhibits both a nematic and a smectic-C^{12} mesophase. Gray and Jones[15] reported the nematic-smectic transition to be 98 °C and the clearing point at 146 °C. When this material was cooled in the presence of a 5000 Hz electric field (5500 V/cm), the long axes of the molecules preferred a direction parallel to the field in the nematic and perpendicular to the field in the smectic phase.

The behavior in the smectic phase did not appear to be an anomalous effect, therefore, the low frequency dielectric anisotropy probably changes sign as this material passes from the nematic to the smectic phase. Since the value for the dielectric anisotropy in the nematic phase was found to be quite small, it is difficult to say much about the change in the dielectric anisotropy at the nematic-smectic transition point.

When *p*-heptyloxybenzoic acid was cooled in the presence of a dc electric field it was observed that a dc field is less effective in ordering the long molecular axes perpendicular to the field than a 5000 Hz electric field. Since this is a smectic-C phase the conductivity may not be a maximum in a direction perpendicular to the long molecular axes. If the direction for the maximum value of the conductivity depends on the tilt angle, an anomalous effect owing to the conductivity anisotropy might account for the results which employ a dc field.

4. Conclusion

The anomalous alignment in the smectic phase appears to be quite similar to that of the nematic phases of *p*-azoxyanisole and *p*-(anisalamino)-phenyl acetate. Although the direction for the maximum values of the conductivity and dielectric constant relative to the long molecular axes in the smectic phase of EMC are not the same as for the corresponding quantities in the two nematic materials, there are many similarities.

1. When observing anomalous alignment, an ordering is preferred such that the conductivity is a maximum in both phases.
2. A critical frequency region which is normally at audio frequencies is associated with both phases and is very sensitive to impurity. Below this region the anomalous effect is observed, and above this region the ordering is believed to be due to the dielectric properties.
3. The degree of alignment produced by a high magnetic field is greater than that produced by a high dc electric field for the nematic materials. A high magnetic field is more effective in aligning the long molecular axes of EMC in a direction perpendicular to the microwave field than a high dc electric field.

The effects associated with the anomalous alignment appear to be very sensitive to impurity. It is possible that some of the impurity in the samples used in this work was essential in order to obtain the results reported. It appears that doping very pure liquid crystals which exhibit a smectic phase could lead to some interesting studies.

When discussing the influence of electric fields on the molecular alignment in the smectic phase, there are many other articles that should be mentioned. Two recent articles,[16,17] which involved EMC and *p*-heptylbenzoic acid, can probably be related to this work. It is difficult to relate the work reported here to other work because of impurity which varies in type and amount. Also different experiments require different sample sizes so surfaces effects, which are not well understood, add to the difficulty.

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