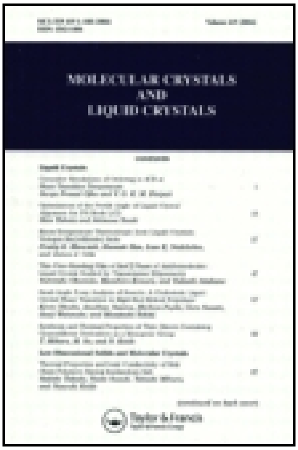

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: J. S. Patel & J. W. Goodby (1987): The Magnitude of the Spontaneous Polarization in Two Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals, 144:5, 117-125

To link to this article: http://dx.doi.org/10.1080/15421408708084208

*Mol. Cryst. Liq. Cryst.*, 1987, Vol. 144, pp. 117–125
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Printed in the United States of America

# The Magnitude of the Spontaneous Polarization in Two Ferroelectric Liquid Crystals

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(*Received October 21, 1986*)

The spontaneous polarization was measured for two chemically isomeric ferroelectric smectogens that have different phase sequences. The two compounds, S-4-(3,'7'-dimethyloctyloxy)phenyl 4-n-decyloxybenzoate and S-4-n-decyloxyphenyl 4-(3,'7'-dimethyloctyloxy)benzoate differ only in the direction of the central ester linkage. Thus, both materials have similar dipolar characters. The first material exhibits a smectic A to smectic C* phase transition, whereas the second exhibits a cholesteric to smectic C* phase change. The optical tilt angle for the first compound saturates, close to 22 degrees in the smectic C* phase, whereas the second has a relatively large temperature independent value of approximately 45 degrees. Concomitantly, the magnitude of the spontaneous polarization of the first material is less than that of the second. The temperature dependence of the polarization of these materials was also measured. It is concluded for materials that are isomeric that the relative size of the polarization is dependent on the magnitude of the tilt angle in the ferroelectric phase, however a quantitative relationship could not be established.

## INTRODUCTION

Tilted chiral smectic liquid crystals, because of reduced symmetry, can exhibit ferroelectricity.[1,2] Although symmetry considerations are used to predict the existence of ferroelectricity in these phases, they unfortunately give no information concerning the magnitude of the spontaneous polarization. However, the size of the spontaneous polarization is an important indicator of the *apparent* strength of the ferroelectric properties. The magnitude depends on several factors such as the size of the dipole moment at the chiral center, the degree to which rotations of the molecule and the chiral center are hindered, and the degree of the coupling between the dipole at the chiral center with the dipoles of the rest of the molecule.

The rotation of the molecule is hindered in chiral as well as non-chiral molecules, partly due to the tilting of the molecules with respect to the layer planes. In non-chiral systems this factor alone is not sufficient to induce ferroelectricity, because the barrier to molecular rotation is symmetrical about the long axes of the molecules. When the constituent molecules are chiral, the symmetry associated with the rotation of the molecules about their long axes is broken, thus leading to ferroelectric behavior.

In this article polarization and tilt angle measurements of two materials that were designed to be isomeric, and exhibit different phase sequences are reported. By changing the direction of the central functional group it is possible to obtain materials with different phase sequences and different tilt angles.[3] One of the materials, S-4- (3,'7'-dimethyloctyloxy)phenyl 4-n-decyloxybenzoate (A) possesses a smectic A to smectic C* transition which, by the virtue of being a second order phase transition, shows a tilt angle variation from zero to about 22 degrees. The second compound *S*-4-n-decyloxyphenyl 4-(3'-7'-dimethyloctyloxy)benzoate (B) has a first order phase transition from a cholesteric to a smectic C* phase, with a tilt angle that grows abruptly from zero at the phase transition to 45° and remains constant over the entire temperature range of the smectic mesophase.

## EXPERIMENTAL

The materials used in this study are shown in figure 1, along with the phase transition temperatures. The polarization measurements were carried out using a triangular waveform and monitoring the current flow through the circuit.[4] The liquid crystal cells had an electrode area of $0.25 \times 0.25$ cm$^2$. The cells were made using standard photolithography techniques using indium-tin-oxide coated glass. The cell spacing was $9.0 \pm 0.2$ microns obtained by using fiber spacers. The alignment methods for the two cells were different, the details for which have been described previously.[5,6] Briefly, for the material with smectic A to smectic C* phase transition, the alignment was produced by coating both surfaces with poly-1-4-butyleneterephthalate and buffing one surface in a single direction. For this class of material the layers form in the A phase perpendicular to the buffing direction. The orientation of the layer direction with respect to the buffing axis is essentially retained when the material is cooled into

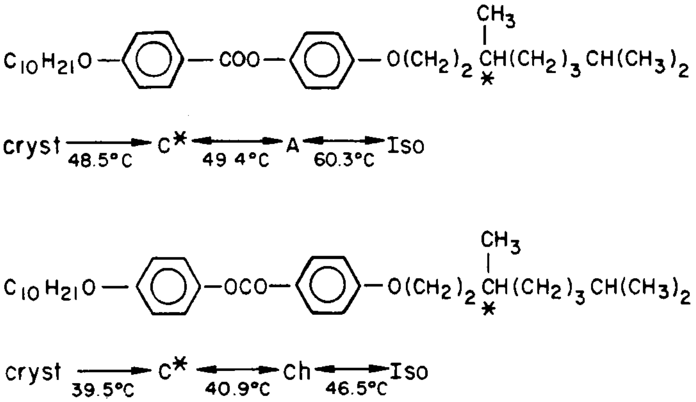

FIGURE 1 The structures of the liquid crystals and their transition temperatures.

the smectic C* phase. For the material with the cholesteric to smectic C* transition, in addition to the above treatment, a slowly varying AC electric field is applied in order to obtain a well-aligned sample.[6] In this case, however, the angle of the layer direction with respect to the buffing axis is essentially equal to the tilt angle of the phase. The sample temperature was controlled using a Mettler FP52 microfurnace in conjunction with a FP5 control unit.

## RESULTS

The detected current through the circuit shows a distinct hump which appears with the onset of the phase transition to the smectic C* phase. This hump corresponds to the additional charge required to reverse the polarization, as the polarity of the applied field is reversed. It was found that the size of the measured polarization depends on the magnitude of the applied peak voltage of the trianglar wave. However, above a certain voltage the polarization saturates to a constant value corresponding to complete polarization reversal. All of the data presented here was obtained at voltages well above this saturation level. At higher voltages additional current peaks are observed that persist in the non-ferroelectric phase, and are therefore not associated with ferroelectric polarization reversal. These peaks, which are structured, are possibly due to ion migration and collection at the cell surfaces.

The results of the polarization measurements are shown in Figure 2. As expected, material A shows a gradually changing polarization

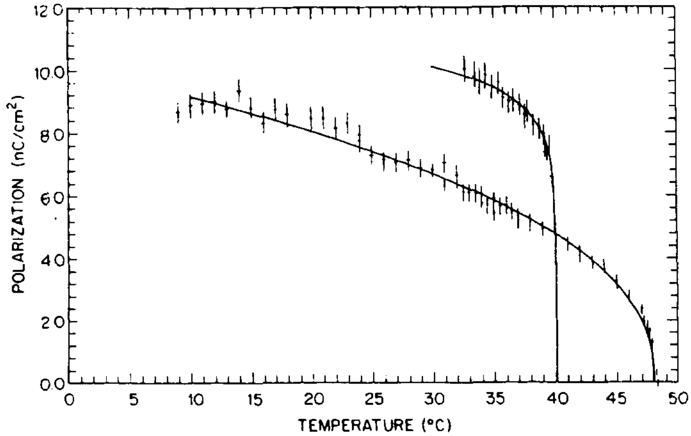

FIGURE 2 Temperature dependence of the polarization. The solid line represents a least square fit to the power law expression as described in the text.

that starts from zero and continuously increases as the temperature is decreased. Material B on the other hand shows an abrupt change from zero to about 8 nC/cm$^2$ at the Ch-C* phase transition, consistent with the discontinuous nature of a first order phase transition. A power law expression of the type $P = P_0(T_c - T)^\alpha$ clearly shows an excellent fit to the data for both materials. Since the certainty with which ($\alpha$) could be determined depends on the value of $T_c$, the uncertainty in the value of ($\alpha$) is primarily due to the accuracy of the temperature measurements. The value of ($\alpha$) for compound A was found to be 0.42 ± 0.02 whereas the corresponding value of $P_0$ was found to be 2 ± 0.2. In fitting the data for compound B to the power law expression of values of $\alpha = 0.09 \pm 0.02$, and $P_0 = 8.3 \pm 0.2$ were obtained.

Optical tilt angles for these two materials also were determined. In the case of material A, the tilt angle was determined from the value of the microscope stage rotation required to bring the specimen into extinction when viewed between crossed polarizers after polarity inversions. The optical tilt angle is equal to half the stage rotation between extinction obtained by reversing the applied electric field. It was found that below ±5 volts the measured value depended on the magnitude of the applied electric field, but above this value the optical tilt angle saturates. Representative data are shown in figure 3 for which the position of the microscope stage for optically extinct states with respect to extinction in A phase is plotted as a function of temperature for both polarities of the voltage. The open circles

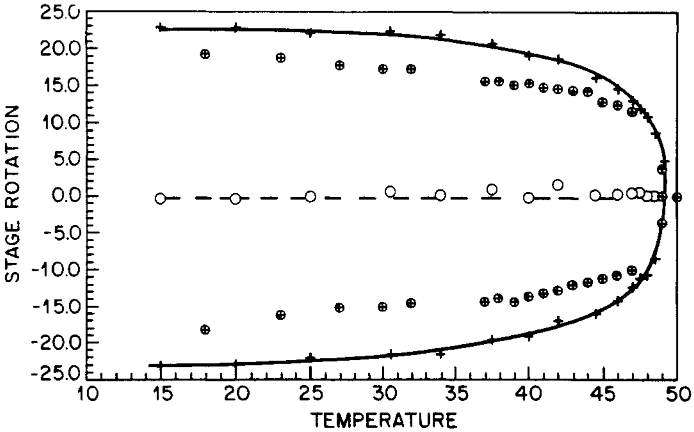

FIGURE 3 Temperature dependence of the tilt angle. Data above saturation voltage (5v) is represented by +, and below saturation (2v) by ⊕. The open circle represents the mean value for the 5V data.

represent the mean value of the stage rotation at a given temperature for positive and negative voltages, when the applied voltage is above saturation. The solid line through the data is the least square fit through these points which shows that the two optical states are symmetrically disposed about the extinction position in the A phase, i.e., the direction parallel to the buffing axis. When a similar procedure is employed for data obtained below the saturation voltage, it is found that the mean value is slightly skewed towards one of the states, presumably due to asymmetry introduced by buffing only one of the surfaces of the cell. Figure 4 shows a log-log plot of the optical tilt angle versus reduced temperature. The data clearly shows that although the power expression $\theta = \theta_0(T_c - T)^\beta$ is useful, the fit is not particularly good. The value of $\beta$ was determined to be $0.20 \pm 0.03$ with the corresponding value of $\theta_0 = 12 \pm 1$.

In the case of compound *B*, the tilt angle was found to be almost temperature independent. The tilt angle was determined by measuring the angle that the dechiralization lines made with respect to the buffing axis. This is because in this class of materials, the layered structure forms so that the molecules align parallel to the buffing axis. Thus, the layers tilt with respect to this axis at an angle equal to the tilt angle. When the temperature of the sample was altered, the measurement of the tilt angle was preceded by removal of the dechiralization lines with a slowly varying AC electric field for several minutes. This was done in order to remove the pinning centers that prevent the reorientation of the layers. This method of determining

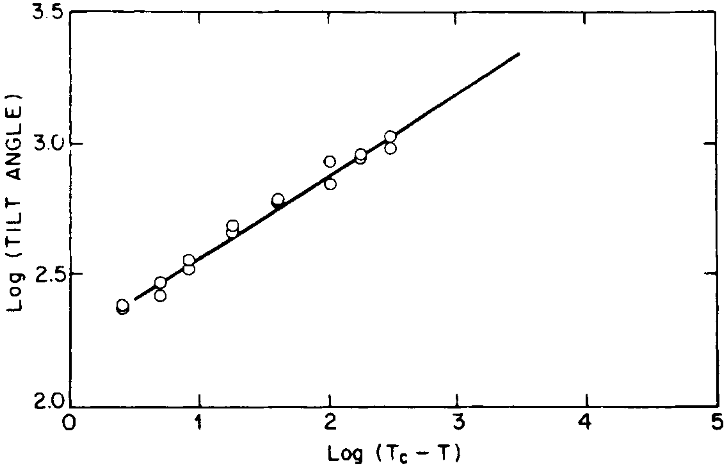

FIGURE 4 Log-Log plot of the tilt angle versus temperature.

the tilt angle was independently confirmed by measuring the reorientation of the optic axis in the presence of an applied electric field. Using both these methods it was determined that the tilt angle changes from about 46° ± 1.5 at 39°C to about 44° ± 1.5 at 29°C.

## DISCUSSION

The second order nature of the smectic A to smectic C* phase transition allows the use of Landau theory to describe the properties of the system in the vicinity of the phase transition by using appropriate order parameters. However, this approach in the case of liquid crystals is thought to be valid only few tenths of a degree away from the phase transition.[7] Nevertheless, in order to compare different materials, it is highly desirable to parameterize the temperature dependence of the polarization and the tilt angle by using some simple expressions. In this study, an expression similar to that used to describe critical behavior, is employed to characterize the properties of the system by an equation of the type $\zeta = \zeta_0(T_c - T)^\eta$ over several tens of degrees. This kind of a behavior has been observed by several other workers,[8,9,10] both for the optical tilt angle and the spontaneous polarization. It is interesting to note that the theoretical models[11] for a material with a smectic A to smectic C* phase transition predict the values of the critical exponent to be 0.5. Other modified models,[12] however, which take into account the fluctuations of the order parameter, give a value of the critical exponent of 0.37.

The experimentally observed value $\alpha = 0.42$ for compound A is in close agreement with these theoretical predictions. Although the temperature dependence of the tilt angle also exhibits a power law dependence, the value of the exponent $\beta$ is different from that obtained for the polarization data. This result is different from earlier observations made on the ferroelectric liquid crystal DOBAMBC.[10] In this material the exponent for both the polarization data ($\alpha$) and the tilt angle data ($\beta$) were found to be the same within the experimental error, and hence it was concluded that the magnitude of the polarization was directly proportional to the tilt angle. However, even in DOBAMBC, the ratio of $P/\theta$ deviates significantly close to the phase transition and has been attributed to the anomalous temperature variation of the helical pitch.[13] While the polarization data for material B can also be represented by the expression $P = P_0(Tc - T)^\alpha$, such a fit is meaningless from a Landau theory point of view, since the transition from the cholesteric phase to the smectic C* phase is first order as shown by differential scanning calorimetry. However, such a fit does aid in parameterizing the data for this compound. It is interesting to note that, for material B, while the polarization clearly shows a temperature dependence in the smectic C* phase, the tilt angle does not show any change over the same temperature range, within the experimental error.

For material A the poor fit of the tilt angle data to $\theta = \theta_0(Tc - T)^\beta$ is partly due to the uncertainty in the measurements, however the difference between the exponents for the polarization and tilt angle material A is real. This difference is not surprising since there appears to be some theoretical basis for this disagreement, at least close to the phase transition.[14] Furthermore the term "tilt angle" is ambiguous and could mean either the tilt angle measured by optical means as performed in this study, or else it could mean the tilt angle determined by X-ray measurements.[15] These two types of tilt angles do not necessarily agree with each other and it suggests that the rigid rod model used to represent the molecule in mean field theories is probably inappropriate as the molecules may in fact be zig-zag shaped.[16]

On a qualitative basis it is possible to understand the relationship between the tilt angle and the polarization if one assumes that the increased tilt angle causes a more hindered rotation and thus a larger polarization. Such an argument however fails for the material B which shows a negligible tilt angle variation with temperature but shows a considerable change in the magnitude of the polarization. In this case it is possible that the coupling of the chiral moiety of the molecule with the rest of the molecule changes with temperature while maintaining a constant the tilt angle. Clearly other factors influence the degree of hindered rotation, these include the intermolecular separation distance, and weak chemical interactions such as hydrogen bonding which are temperature dependent. Change in the density of the system, while maintaining constant tilt angle, can also account for the temperature dependence of the polarization.

## CONCLUSION

In general, a universal relationship between tilt angle and polarization cannot be expected, because while the tilt angle influences the degree of hindered rotation, it is not the only relevant factor. Consequently a quantitative comparison even between these two chemically similar materials cannot be made. However it can be seen that the size of the polarization for compound B, that has the larger tilt angle, does in fact have a larger polarization, indicating that tilt angle nevertheless does play a role in determining the magnitude of the polarization.

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