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Measurement of spontaneous polarization in ferroelectric smectic liquid crystals

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This paper presents measurements of spontaneous polarization made on two ester-bridged materials (SCE1 and CE8). The two materials are chosen to be representative of long pitch (SCE1) and short pitch (CE8) materials. The measurements were made by two different methods, Diamant bridge and field reversal; these methods are compared and the results shown to be in good agreement. The variation in results between different samples of these materials is discussed and the results compared (where possible) with the work of other authors. Special attention is paid to the variation which occurs between the published spontaneous polarization measurements of different authors. The reasons for this variation are examined and variation in sample alignment and the determination of the transition temperature by different authors are shown to be major causes.

1. Introduction

The symmetry arguments of Meyer [1] (cf. also de Gennes [2]) have shown that any tilted smectic phase which is composed of chiral molecules should exhibit ferroelectric properties, since the local symmetry of these phases induces a parallelism of the electric dipole moments in each smectic layer. There is, however, associated with these smectic liquid crystal phases an intrinsic helical structure which results in the projection of the director onto the plane of the layer, **c**, rotating from layer to layer about an axis parallel to the layer normal. The presence of the helical structure, therefore, results in the plane of polarization (which is parallel to the layers and normal to the **c** director) rotating from layer to layer. Thus a non-zero average polarisation is reached only in samples in which the helical structure is unwound. This unwinding is effected by surface interactions (predominant in thin samples) and electric fields (predominant in thick samples). In this context a thin sample is one in which the pitch is greater than the cell thickness.

Measurements of the spontaneous polarization made on common ferroelectric S_C^* compounds such as DOBAMBC (*p*-decyloxybenzylidene *p*′-amino 2-methylbutyl cinnamate) often vary substantially between authors. Figure 1 shows a representative selection of the results obtained by various authors for this compound [3–7]. Although some spread of this data may be accounted for in the case of DOBAMBC by the unstable nature of the Schiff's base linkage in the molecular core, this alone cannot account for all of the large variations. The reasons for such variations observed in this parameter are examined in this paper.

Experiments were carried out on two ester bridged compounds (SCE1 and CE8 supplied by BDH chemicals Ltd) which are relatively stable and this removes variations due to the unstable nature of a material. The chiral smectic C mixture SCE1

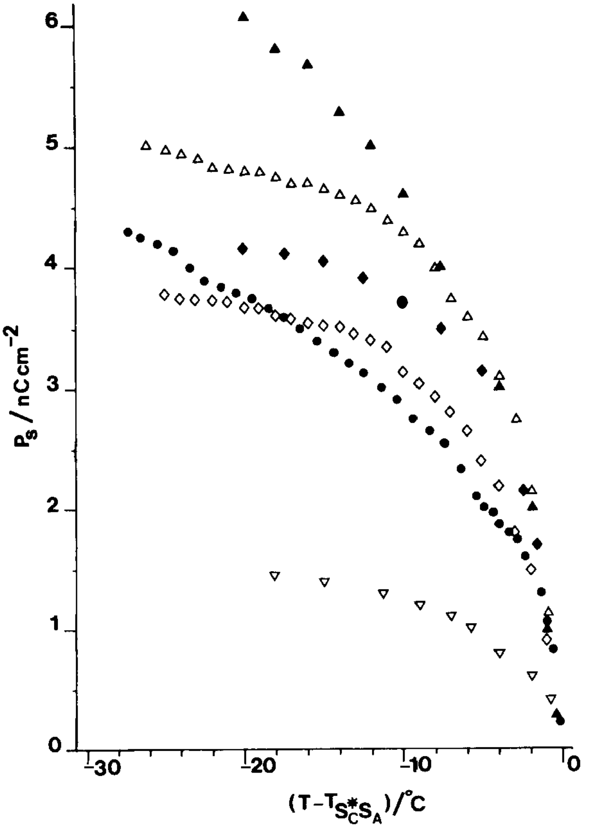

Figure 1. Various measurements of P_s for DOBAMBC.

exhibits relatively large values of spontaneous polarization, a long pitch in the S_C^* phase (~ 15 μm) and a wide S_C^* phase encompassing room temperature. This material also exhibits the property of aligning reasonably consistently with the alignment layers used. This property is assisted by the presence of partially compensated cholestric pitch in the phase sequence of this compound. In contrast to SCE1, CE8 has a relatively low P_s, a short pitch (~ 2–3 μm), a relatively narrow S_C^* phase and reasonable alignment properties. The two compounds chosen, therefore, are considered to show sufficient variations in the material parameters to be reasonably representative of ferroelectric smectic C liquid crystal materials.

2. Experimental method

Cells for the polarization measurements were made of two ITO coated glass plates spaced with mylar to obtain a liquid crystal layer of uniform thickness. The ITO conducting layers are etched to define an active cell area (determined photolithographically) of about 10 mm square. The cells were filled by capillary action and alignment of the sample was achieved using rubbed surface coatings of polyamide or polyimide. Both of these coating materials gave good results and no difference in performance was observed between them. The rubbed layers reproducibly produced the so-called homogeneous bookshelf geometry (in which the smectic layers are approximately perpendicular to the cell walls) in the samples. The two uniform states of the polarization field (up and down) which can be switched (at very high speed) under the influence of an applied field, are usually formed in a sample of this geometry when the intrinsic helical structure is unwound. During the measurements the sample was observed with a polarizing microscope. The sample temperature was controlled to within 0·1°C by a Mettler FP82 hot stage. The value of spontaneous polarization was measured by different direct measurements to assess the consistency of these measurement techniques. These methods were Diamant bridge [8] and compensated field reversal [9].

2.1. *Diamant bridge*

This method was originally developed by Diamant *et al.* [8] for the measurement of spontaneous polarization in solid ferroelectrics. The circuit is shown in figure 2. The bridge consists effectively of two Sawyer–Tower [10] circuits in parallel, one of which contains the sample and the other of which is a resistor–capacitor network. The method used is based on a technique of hysteresis compensation. The X and Y components of the hysteresis loop are formed by the drive voltage from the oscillator and the voltage difference which appears between the two reference capacitors, respectively. This voltage difference represents the difference in current flow through the sample and the compensation network during voltage switching and is measured using a unity gain amplifier as an impedance matching device.

In this method the compensation network is adjusted to give a suitable hysteresis loop at any given temperature. The spontaneous polarization at any given temperature is then determined from the balanced hysteresis loop and is given by the following equation:

$$P_s = C_0(V_{0B})_c/2A,$$

where A is the active area of the sample, $(V_{0B})_c$ is the maximum peak to peak voltage of the compensated hysteresis loop and C_0 is the value of the fixed capacitor in the arm of the bridge containing the sample.

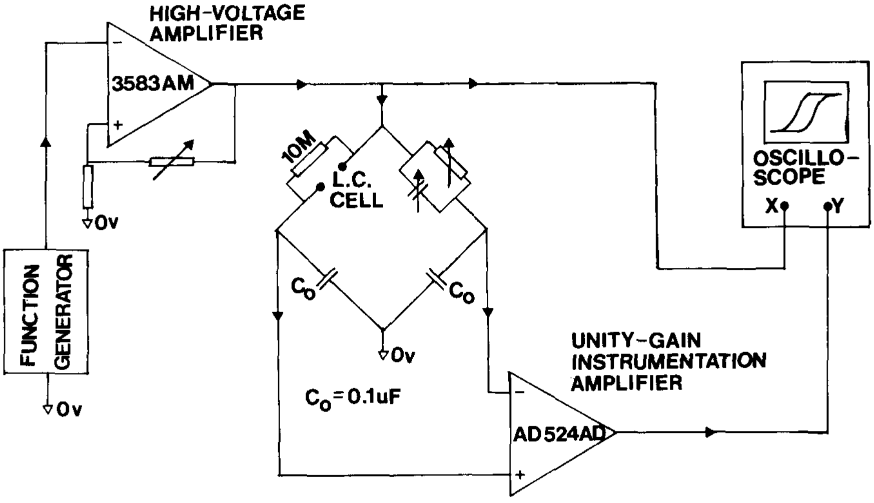

Figure 2. The Diamant bridge circuit.

2.2. *Field reversal*

Any method [11–13] of measuring spontaneous polarization which measures the transient current resulting from polarization reversal in the sample requires the large current components due to ion flow and charge accumulation within the sample to be subtracted from the output current. This current consists of three components

$$I_{\mathrm{total}} = I_{(\mathrm{C})} + I_{(\mathrm{P})} + I_{(\mathrm{I})}, \tag{1}$$

where $I_{(\mathrm{C})}$ the current due to charge accumulation in the cell, $I_{(\mathrm{P})}$ is the current due to realignment of polarization and $I_{(\mathrm{I})}$ is the charge due to ion flow in the sample. Assuming that the sample may be represented by a resistor (R_{p}) and a capacitor (C) in parallel, equation (1) becomes

$$I_{(\mathrm{total})} = CdV/dt + dP/dt + V/R_{\mathrm{p}}, \tag{2}$$

and therefore

$$I_{(\mathrm{background})} = V/R_{\mathrm{p}} + CdV/dt. \tag{3}$$

Miyasato *et al.* [11] and Skarp *et al.* [12] have taken the approach of calculating the background current component numerically using equation (3) and subtracting the values obtained from the stored experimental data. The remaining current component due to the polarization realignment is then further processed to evaluate the magnitude of the total charge transferred within these current pulses. In the preliminary stages of the present study the field reversal methods of Martinot-Lagarde [13] and Miyasato *et al.* [11] using square and triangular drive waveforms, respectively, were studied as a means of measuring the current component due to the polarization. However, a modification of the method was made in the present study to achieve a reduction in the complexity of the processing required. Compensating discrete components were used in a parallel circuit to produce an equivalent current to the background current given by equation (3). This background current is then subtracted electronically from the current produced in the sample during switching. The charge in the remaining current component due to the polarization realignment may then be derived either by digital or by analogue techniques. In the present system an analogue integrator was employed.

A block diagram of the experimental set-up is shown in figure 3; for a more detailed account of this instrument see [9]. The drive waveforms were generated by a conventional function generator with a high voltage amplifier producing an output voltage of 300 V peak to peak. The sample and background currents were determined from the voltage drops across 100 k resistors which are small in comparison to the sample resistance. These voltages were fed into the inputs of a differential amplifier of which the output then represents the polarization current component.

It may be of interest to note that the compensated circuit employing an integrator with a slowly varying drive voltage may be considered to be similar to a Diamant bridge circuit since both circuits measure the total charge flow during the polarization realignment by means of a series capacitor. In the compensated field reversal curcuit the presence of the current sensing resistors allows the polarization realignment current component to be examined readily during the actual switching process. All field reversal measurements of the polarization allow the time dependence of the polarization realignment current to be observed during switching. It is this feature that is considered to separate these measurements conceptually from a Diamant bridge where the voltage appearing across a reference capacitor which represents the

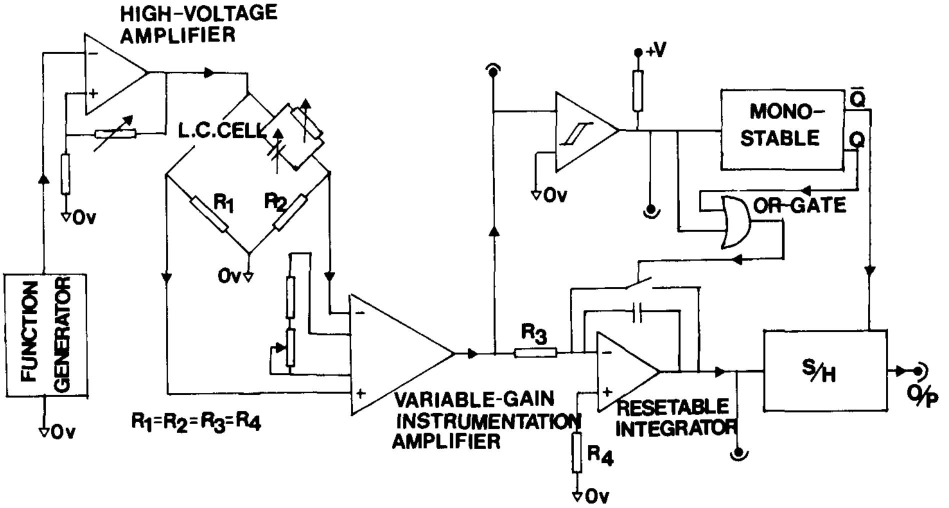

Figure 3. Block diagram for the field reversal instrument.

charge flow in the sample during switching is displayed as a function of the drive voltage to form a hysteresis loop.

3. Results

The Diamant bridge results for sine wave and triangular voltage drive waveforms are mutually consistent to a very high degree. Figure 4 shows the typical consistency obtained in measurements taken with the Diamant bridge for both waveforms for a 12 μm sample of CE8.

The field reversal method also yields results which show a very high degree of independence of drive waveform. Figure 5 shows results obtained with a 2 μm sample of SCE1. This figure also illustrates the typically high degree of consistency between measurements on the same sample between Diamant bridge and field reversal methods. This consistency extends to both the high and low P_s materials and even to samples in which the alignment is poor. Figure 6 shows results for two CE8 cells, one of which was inadequately aligned, deliberately to produce a focal conic structure as a means of establishing that the agreement between methods does not occur only in well-aligned samples.

The measured values of P_s appeared to be unaffected by the method employed to unwind the pitch, namely surface interactions for SCE1 ($p \gg d$) or applied electric fields for CE8 ($d > p$)). Furthermore these P_s values did not seem to depend on the choice of measurement technique.

The results presented here tend to lead to the conclusion that the wide spread in the published direct measurements of spontaneous polarization is most unlikely to be due to the different methods of measurement used by the different authors. Our present results suggest that the spread of published values is most likely due to variation in the alignment and the determination of $T_{S_C^*S_A}$. Determination of this transition temperature is more important with well-aligned samples. $T_{S_C^*S_A}$ has been determined by some authors using batch measurements of material (for example, differential scanning calorimetry) and by others using optical measurements on individual cells. It is established that for experimental samples $T_{S_C^*S_A}$ shows a

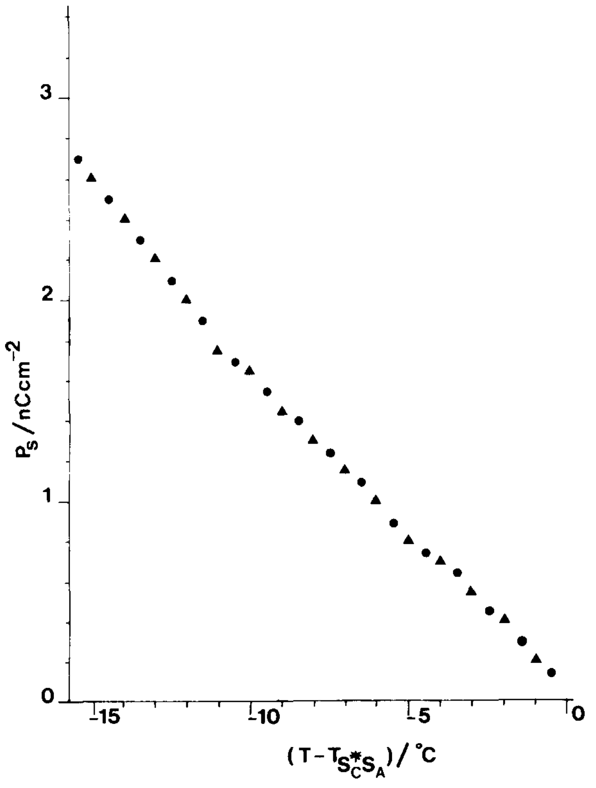

Figure 4. Diamant bridge determination, a comparison of drive waveform dependence; 12 μm CE8 sample; ●, sinusoidal drive; ▲, triangular drive.

dependence on cell thickness, alignment and the electroclinic effect which is evidently not accounted for when relying on a bulk measurement of $T_{S_C^*S_A}$. Differing spontaneous polarization results from cells from the same thickness range can be brought nearer coincidence by making quite small changes in the value of $T_{S_C^*S_A}$ used to determine the reduced temperature which suggests that the inaccuracy in the determination of this parameter may be partially responsible for the spread in the results reported.

Alignment, however, is the main cause of variation. Therefore, in order to ascertain the variations in P_s due to this parameter, measurements of P_s against cell thickness were made. Figure 7 shows the variation of P_s with cell thickness for CE8. This demonstrates that there is very little variation of P_s with cell thickness for well-aligned samples. It was found, however, that the required degree of alignment is more readily acheived in thinner samples.

Figure 8 shows the extent to which variation can occur in otherwise similar samples with varying degrees of alignment. A lower value of spontaneous polarization is to be expected in poorly aligned samples since the presence of small-scale focal conic texture appears to result in a smaller effective switching area than that which would be associated with an otherwise similar well-aligned sample. It can be seen that not only is there the expected large variation between the well and poorly aligned samples but there is also a fairly large variation between the apparently well-aligned samples.

Figure 9 shows the effect of P_s of leaving a CE8 cell overnight in a crystal (or smectic) phase. This shows a significant reduction in the P_s value which is consistent

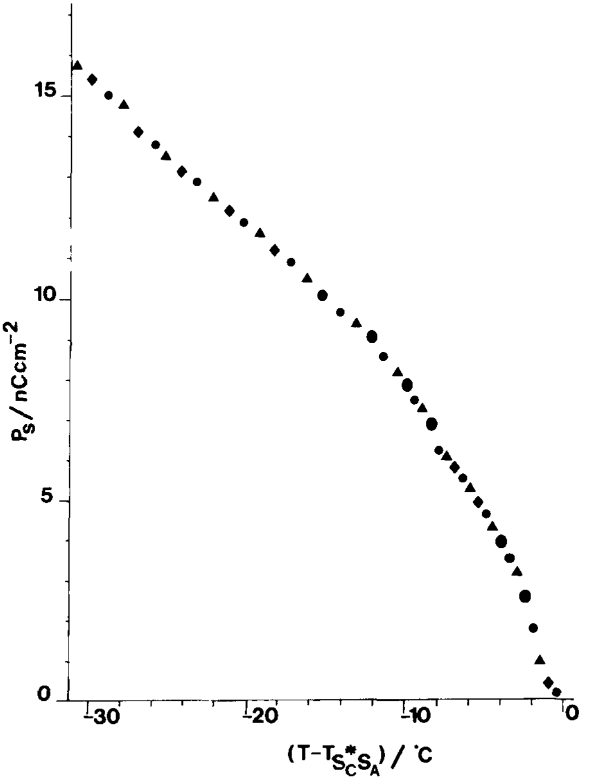

Figure 5. Comparison of P_s measurements; 2 μm SCE1: ●, Diamant bridge field reversal; ◆, sinusoidal drive; ▲, triangular drive.

with the deterioration in alignment which was also observed. This sort of effect is not observed in SCE1 due to the different phase sequence in this material.

Clark and Lagerwall [14] have recently reported the results of high resolution X-ray experiments which show that the smectic layers within thin ferroelectric samples, while substantially planar, are often tilted with respect to the normal to the cell surface. The presence of such a tilted layer structure is known to influence the director field boundary condition and the consequent variation between smectic layer orientation in samples fabricated using different alignment techniques further complicates the comparision of the P_s measurements by different authors.

3.1. *Variation of P_s with temperature*

The variation of P_s with temperature was investigated and compared with the temperature dependence of tilt angle to form an assessment of the widely used formula

$$P_s = P_0\theta;$$

it is customary to assume that

$$\theta \propto (T_{S_C^*S_A} - T)^{\beta}$$

and hence that

$$P_s \propto (T_{S_C^*S_A} - T)^{\beta}.$$

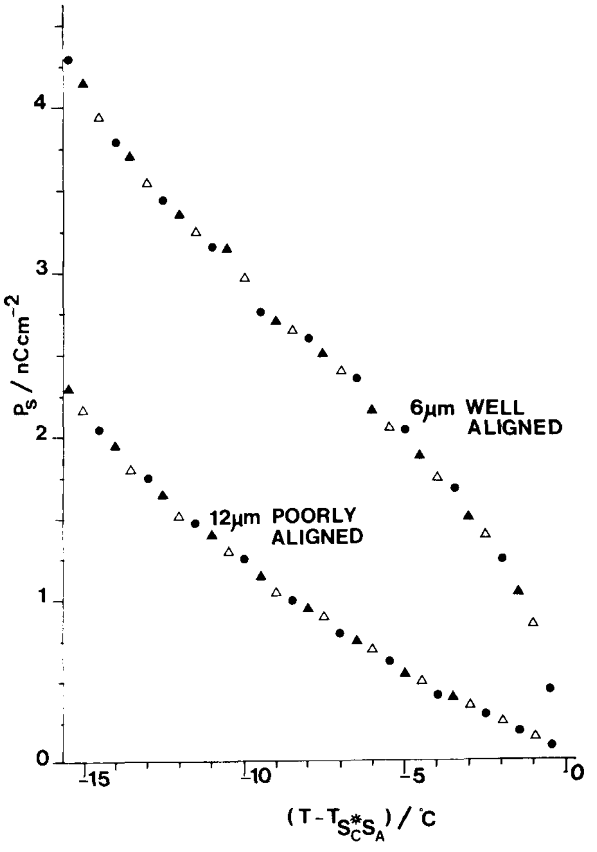

Figure 6. Comparison of P_s measurements; CE8; ●, Diamant bridge field reversal; △, sinusoidal drive; ▲, triangular drive.

The relationship between the optical tilt angle and temperature was investigated for CE8 and SCE1 according to

$$\theta = \theta_0(T_{S_C^*S_A} - T)^{\beta},$$

where β is obtained from the gradient of a log θ versus log $(T_{S_C^*S_A} - T)$ plot after a least-square adjustment of the data. The least-square fitting was carried out on the region of the log–log plot where β is apparently constant. This is not the case in the immediate vicinity of $T_{S_C^*S_A}$ where as θ approaches zero there is no component of the molecular director in the smectic layer planes and the concept of a spiralling **c** director on which the phase is modelled ceases to be valid since the length of the rotating **c** director is proportional to sin θ which also tends to zero. These least-square fits exhibited correlation factors around 0·99 or better. The results indicate that the power law appears to be valid away from the smectic C–smectic A phase transition. The calculated values of β for the tilt angle (0·41 for CE8 and 0·47 for SCE1) are within the experimental range of 0·35 to 0·50 expected from the work of Martinot-Lagarde *et al.* [15] and Goossens [16].

The relationship between the spontaneous polarization and temperature was also investigated for CE8 and SCE1 according to

$$P_s = A(T_{S_C^*S_A} - T)^{\beta}.$$

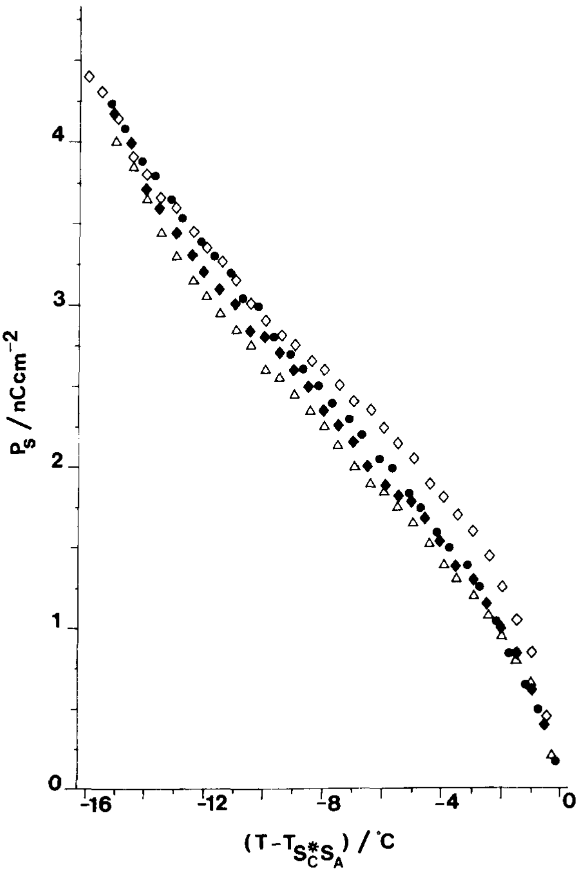

Figure 7. The dependence of P_s on the cell thickness; CE8; ◇, 6 μm; ●, 12 μm; △, 25 μm; ◆, 50 μm.

The values of the exponent were calculated from the slope of $\log P_s$ versus $\log(T_{S_C^* S_A} - T)$ after least-square adjustment of the data. The correlation factor in each case was greater than 0·99 and again the power law seems to be valid in the temperature region away from $T_{S_C^* S_A}$. Thus, in this region the present work indicates that these relationships hold. It cannot be reliably assumed, however, that the exponent is the same in each case since, although β is about 0·40 for DOBAMBC (which is consistent with the published data of other authors), the results presented here indicate that the values are different for CE8 (0·41 for the tilt angle and 0·68 for P_s) and SCE1 (0·47 for the tilt angle and 0·65 for P_s).

The temperature dependence of these parameters was also examined for a changing power law exponent in the temperature interval near to the ferroelectric transition. Least-square fits with correlation factors better than 0·99 made on data acquired in a temperature interval of a few degrees indicate a significant change in the exponent for the samples of the commercial mixture SCE1 but not for the samples of CE8. These least-square fits indicated an increased power law exponent for SCE1 samples in this region (0·70 for θ and 1·58 for P_s). The increased temperature dependence of these parameters for SCE1 may be explained by a greater sensitivity of the molecular dipole orientation in this temperature region to strong surface anchoring and applied

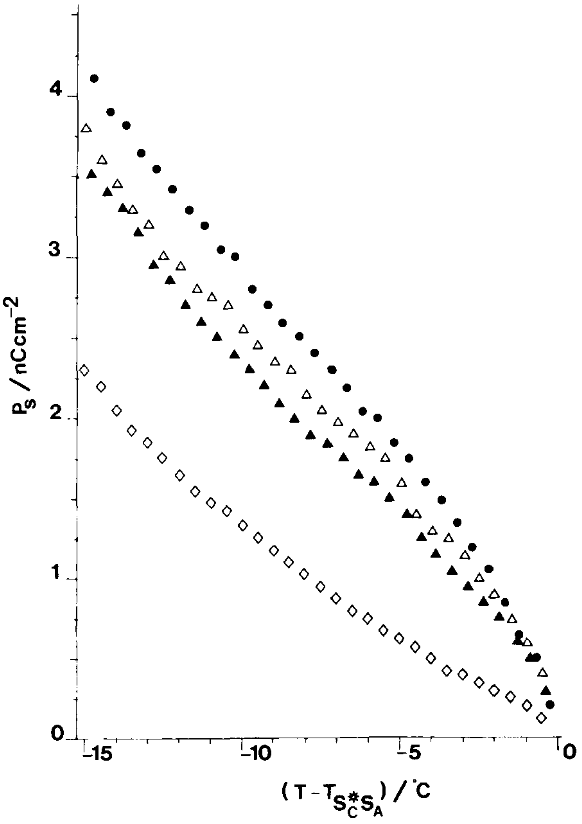

Figure 8. The effect of varying degrees of alignment on P_s; 12 μm CE8 samples; ●, △, ▲, well aligned; ◇, poorly aligned.

fields. From our discussion it seems clear that the expression

$$P_s = P_0\theta$$

is not generally valid.

3.2. *Variation of P_s with field*

No field dependence of the value of the spontaneous polarization was observed during this study provided the applied field was sufficiently strong to align the molecular dipoles. It is known that the measured value of P_s may be field-dependent in samples possessing surface anchoring which is field sensitive (as in cells made from clean glass surfaces) or where measurements are made in the immediate vicinity of the phase transition temperature. The cells used throughout this study, however, employed surface alignment layers and very few measurements were taken within 0·2°C of $T_{S_C^*S_A}$ which Carlsson and Dahl [17] considered to be the outer limit for electroclinic influence.

The measured values of the spontaneous polarization were also found to be independent of the frequency of the drive waveform provided that this frequency was not high enough to prevent the molecular dipoles following the changing field polarity.

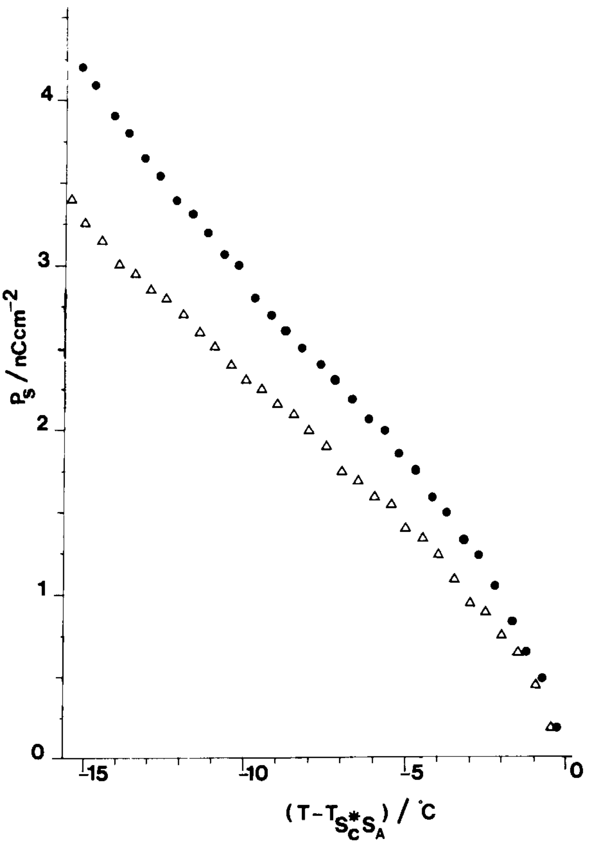

Figure 9. The effect of storage on P_s; ●, 12 μm CE8 sample; △, same sample after storage.

4. Conclusions

Extensive measurements have been made of P_s by several methods on two materials and these have shown that results are consistent between methods but that measurements made with different degrees of alignment may differ significantly. Detailed examination of the present results and those of previous authors has led to the conclusion that the measured value of P_s is highly dependent on the value of $T_{S_C^*S_A}$ used in the calculation. It has been argued that minor differences in the $T_{S_C^*S_A}$ value used can cause major changes in the apparent temperature dependence of P_s when P_s is plotted against reduced temperature.

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