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Measurement of the Kerr effect in cholesteric blue phases

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The electric field induced birefringence within the blue phases and the isotropic phase of several different liquid crystals has been measured. The temperature dependences within the blue phases are found to be strong, characteristically different for each phase, and unlike what is predicted by simple theoretical arguments.

1. Introduction

1.1 *Previous studies*

In recent years the effects of electric fields on the blue phases of cholesteric liquid crystals have been increasingly studied [1-32]. The greatest efforts have been devoted to investigating the electric field-temperature phase diagrams of various materials and mixtures [1-17]. In addition to finding the stability limits of the cubic blue phases which were already known to exist at zero field, new phases with different symmetries, including especially hexagonal, were discovered at high fields [4-17]. The field orienting and faceting effects on small platelets have also been observed and studied and have provided insights into the lattice symmetries of the blue phases [18-21]. Finally, the measurement of the variation of the lattice parameters with field by means of Bragg reflection has given information concerning the structural properties of the blue phases [3, 11, 22-26].

In all of the above cited studies the observation of the blue phases has been made parallel to the direction of the applied electric field, and the field induced birefringence could therefore not be studied. One of these experiments, however, did measure the *change* in index of refraction with applied field [27] and another reported evidence for a small field induced birefringence when looking parallel to the field direction, which is evidence for the production of a *biaxial* structure [28] in contrast to all the other experiments which evidently have yielded uniaxial distortions.

Recent review articles which discuss electric field effects have been given by Stegemeyer *et al.* [29] and by Crooker [30].

1.2. *This study*

Our experiments have been designed to directly detect the electric field induced birefringence—the Kerr effect—by observing the samples perpendicular to the applied field. This important electromechanical property will, we hope, give insights into the structural properties of the blue phases in addition to what has already been learned through the studies of their lattice parameters. Also, we are able to extend our measurements into the isotropic phase, which gives important information concerning the critical phase transition behaviour of these systems, which complements the results obtained from light scattering [33].

As far as we are aware, only the experiments of Gerber [31] and of Beevers *et al.* [32] have previously looked at the Kerr effect in blue phases. But both of these studies differ from our work in that the blue phase(s) could not be clearly identified owing to the very small pitch in the case of Gerber and the lack of platelet textures in the case of Beevers *et al.* Nevertheless there are similarities in the magnitudes of the Kerr effects and the temperature dependences reported in these two studies and ours.

2. Experimental method

Our apparatus and experimental approach as applied to nematic liquid crystals have already been described in great detail elsewhere [34], so this discussion will be brief and will only highlight the features which are different and pertinent to this study of blue phases. Our samples, sandwiched between two glass microscope slides, were examined on the hot stage of a polarizing microscope. Carefully milled inconel plates of about 3 mm thickness were used as both spacers and electrodes. This thickness was chosen so that the optical path difference would be large enough to measure. The spacing of the electrodes perpendicular to the viewing direction was made narrow —about 0·3 mm—so that the applied electric field could be made both large and relatively uniform. Because of these conditions we were not able to see the blue phases with the clarity one is used to in other experiments, although we were clearly able to distinguish between the different phases and to mark the transitions between them.

Also, our experiments have been restricted to fields which were strong enough to elicit measurable effects but not so large as to produce field-induced blue phases. We are primarily concerned in this article with the phase transition behaviour and the physical properties of the blue phases which exist at and near zero field. Future work may be devoted to the higher field blue phases.

As in our previous work, the sample was oriented with the electric field at 45° to the crossed polarizers and the induced birefringence was determined by cancellation with either a $\lambda/32$ or a 6λ compensator, depending upon its magnitude. The sign of the birefringence was deduced by noticing whether the field needed to be oriented parallel or perpendicular to the compensator axis for cancellation.

It should perhaps be noted that the optics of an object which is simultaneously optically active and birefringent can be quite complicated in general; it may look bright when viewed between crossed polarizers because of either or both of these optical properties. For the field strengths used in our experiments, however, the birefringence is overwhelmingly dominant; when the electric field is turned off, or when it is adequately compensated for, the sample is essentially dark. There are, therefore, no particular complications due to the presence of the optical activity of these samples.

3. Results and discussion

3.1. *Cholesteryl nonanoate—the isotropic phase*

The largest part of this paper will be devoted to cholesteryl nonanoate (CN), a material with negative dielectric anisotropy, which we have studied in the greatest

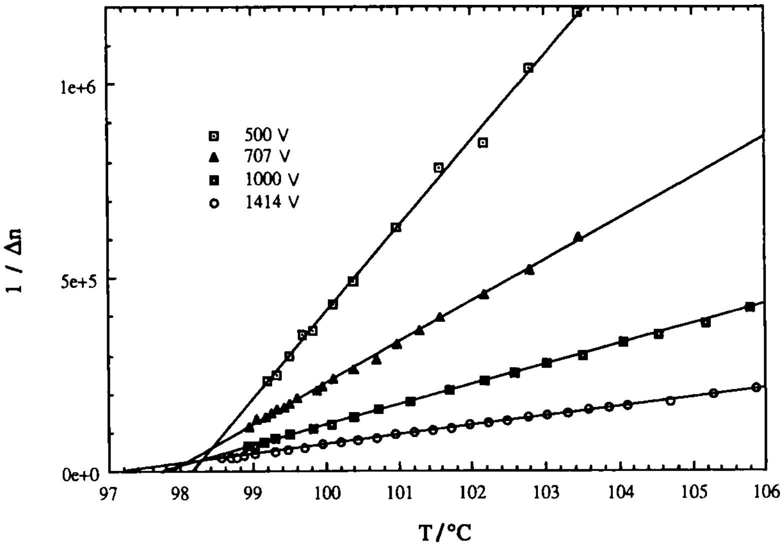

Figure 1. The inverse of the birefringence induced in the isotropic phase of cholesteryl nonanoate by four different applied voltages.

detail. We begin with a discussion of the results found in the isotropic phase, which may be conveniently analysed by means of the second order expansion of the Landau-de Gennes free energy [35–38]

$$F = F_0 + \tfrac{1}{3}AQ_{\alpha\beta}Q_{\beta\alpha} - Q_{\alpha\beta}E_\alpha E_\beta, \qquad (1)$$

where A is temperature dependent, $A = A_0(T - T^*)$, and the order parameter $Q_{\alpha\beta}$ is the anisotropic part of the dielectric tensor

$$Q_{\alpha\beta} = \varepsilon_{\alpha\beta} - \tfrac{1}{3}\varepsilon_{\gamma\gamma}\delta_{\alpha\beta}. \qquad (2)$$

Minimization of this free energy gives the following field and temperature dependence for the birefringence

$$\Delta n \propto \frac{E^2}{A_0(T - T^*)}. \qquad (3)$$

In figure 1 we show the results of measurements made on CN in the isotropic phase at four different voltages, which were chosen so that their squares would differ by factors of two from each other. It is clear that to a high degree of precision the inverse birefringence has the linear temperature dependence predicted by equation (3). It may also be noted that, as the voltage is increased, the temperature T^* towards which the data extrapolate drops to lower values. In theory there should be little or no change in T^* over this range of voltages, and whatever change there is should be towards higher temperatures as the voltage is increased. This decrease is actually an experimental artifact, due to the local Ohmic heating of the sample which causes the local temperature of the liquid crystal to increase somewhat over the value of the hot stage. We had reported this effect in our earlier studies [34] where it was about the same order of magnitude as we see here.

We have corrected for these Ohmic heating effects by shifting all the data so that the T^* values are the same as found for the 500 V sample. At the same time, to verify

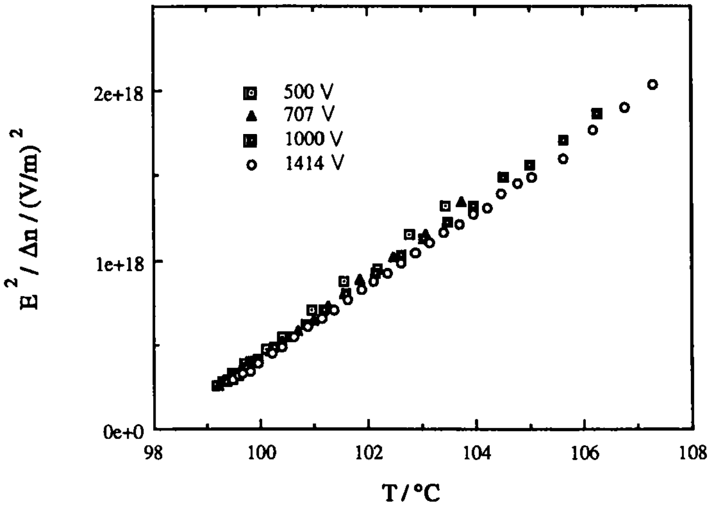

Figure 2. The data of figure 1 scaled by the square of the electric field.

the field dependence predicted by equation (3), we have multiplied the inverse birefringence by E^2 (the electrode gap in this case being 0·474 mm) and display the results in figure 2. The fact that all of these data fall so nearly on the same line is excellent verification of the theoretical prediction of equation (3).

3.2. *Cholesteryl nonanoate—the blue phases*

In figure 3 we present the data taken at an applied voltage of 707 V showing both the isotropic phase and the blue phase regions. It is interesting that the induced birefringence continues to increase within the blue phases, although the temperature dependence is not the same as was found in the isotropic phases. Figure 4 shows the

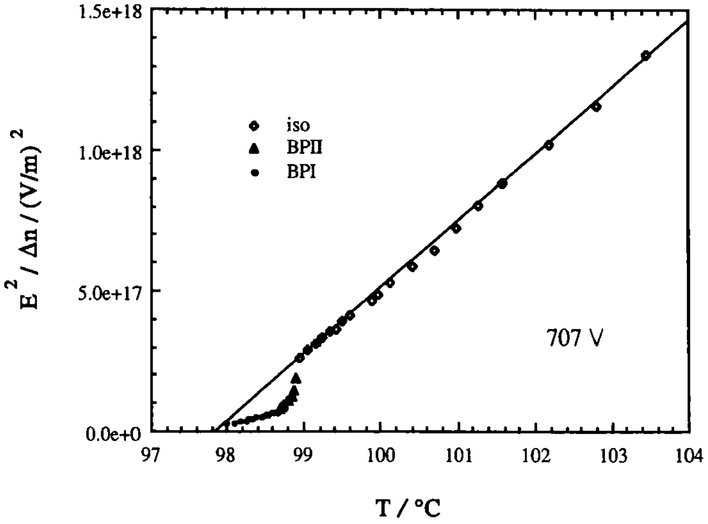

Figure 3. $E^2/\Delta n$ versus temperature for cholesteryl nonanoate showing the blue phase as well as the isotropic regions for an applied voltage of 707 V.

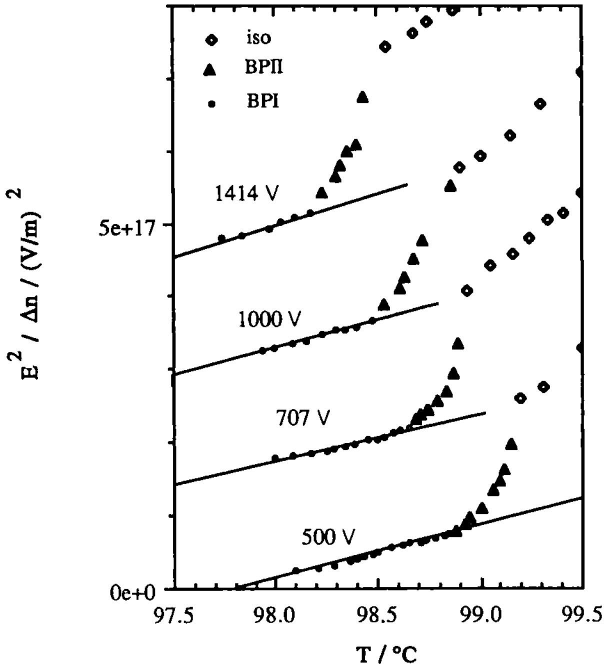

Figure 4. $E^2/\Delta n$ versus temperature for cholesteryl nonanoate—details of the blue phase regions for four different applied voltages. For clarity the data have been displaced vertically by $1{\cdot}5 \times 10^{17}$ V^2/m^2 for each successive voltage increase.

details of the blue phase region for the four different applied voltages. Each of the cubic blue phases exhibits its own characteristic temperature behaviour. The variation is particularly rapid in the BP II region, especially at the transition to the isotropic phase where it is probably discontinuous. Although there is little if any discontinuity at the BP I–BP II boundary, there is an abrupt change in slope. Since the behaviour is approximately linear within the BP I region, we have taken the liberty of fitting these data to straight lines. We know of no theoretical reason for such linear behaviour; this is a highly interesting feature of our data and is suggestive of possible pretransitional critical behaviour associated with the BP I–cholesteric transition similar to what is seen at the isotropic–blue phase transition. One would imagine, however, that if this transition had second order features they would also show up in other features, such as the Bragg reflections, but we have not seen any such indications in any of the results published thus far. We think that this phenomenon deserves further investigation.

We now compare these results for BP I and BP II with the behaviour which might be expected from theoretical considerations. To begin with it must be admitted that it is not entirely obvious how large the Kerr effect and its temperature dependence should be. The coupling to the electric field ought to improve as the order parameter increases. At the same time, however, the elastic constants increase with the order parameter and distortion of the cubic structure should for this reason be harder to achieve. Dmitrienko [39] has presented a phenomenological theory which concludes that these two competing effects cancel each other out and the Kerr effect should be independent of temperature to a first approximation.

On the other hand one can give a quite plausible heuristic argument which reaches a slightly different conclusion, as follows. The distortion of the cubic lattice by the external field is somewhat like the well understood problem of the unwinding of a cholesteric helix by an applied field [35, 37]. Since the lowest order effect should vary as the square of the field, one might then expect that the Kerr effect of a blue phase would be approximately given by

$$\Delta n \cong \Delta n_{\mathrm{nem}} E^2/E_c^2, \tag{4}$$

where E_c is the critical field necessary to unwind the cholesteric and Δn_{nem} is the birefringence, typically about 0·1, of the unwound cholesteric—the nematic. Equation (4) is essentially the estimate given by Lubin and Hornreich [21] for the electric field dependence and the magnitude of the effect. (Their detailed calculations also show the dependence on the specific lattice symmetry and the orientation of the electric field with respect to the basis vectors.)

Equation (4) captures the essence of the competition between effects in that the square of the critical field E_c^2 varies directly with the order parameter and inversely with the elastic constant K. Since K is expected to be proportional to the square of the order parameter, one would expect that the field induced birefringence would decrease somewhat as the temperature is lowered, rather than remaining constant as Dmitrienko has predicted.

Neither prediction agrees with our observation that the Kerr effect *increases* dramatically as the temperature is lowered. This discrepancy might be related to the fact that the calculations of the birefringence have assumed, explicitly in the case of Lubin and Hornreich and implicitly in the case of Dmitrienko, that the dielectric anisotropy is positive, whereas in our material it is negative. Although the mode of distortion may well be different for a negative dielectric anisotropy, the competing roles of order parameter and elastic constant are not altered, and one would not expect the sign of the anisotropy to be the explanation for this behaviour. Certainly the sign of the anisotropy does not seem to affect greatly the magnitude of field necessary to produce a phase transition to another structure [16–18, 40]. We leave this as an open and interesting question.

The prediction that the Kerr effect within the blue phases should vary as the square of the electric field is well verified. It is first necessary, however, to shift the data to compensate for the Ohmic heating effects, as we have already discussed for the isotropic phase. Inspection of figure 4 reveals that the data for each of the blue phase regions can be made to coincide nicely with the proper temperature shift. Note in particular that the lines drawn through the BP I data all have the same slope to within 10 per cent.

It will also be noticed in figure 4 that the range of the various phases is altered somewhat with the applied field. This effect is summarized in the phase diagram of figure 5 in which we plot the transition temperatures, referenced to the value of T^* seen from the isotropic phase, versus the electric field value. The BP I range is seen to shrink as the field is increased, which is similar to what has been found in other systems [1–17, 40].

3.3. *Cholesteryl butyrate and cholesteryl propionate*

Cholesteryl butyrate and cholesteryl propionate are members of the same homologous series that cholesteryl nonanoate belongs to. They have shorter end chains and longer pitches than cholesteryl nonanoate. Cholesteryl propionate is the first member of this series to possess a blue phase, which is BP I, and cholesteryl butyrate is the first to have both BP I and BP II. In figure 6 we plote data for cholesteryl butyrate for one

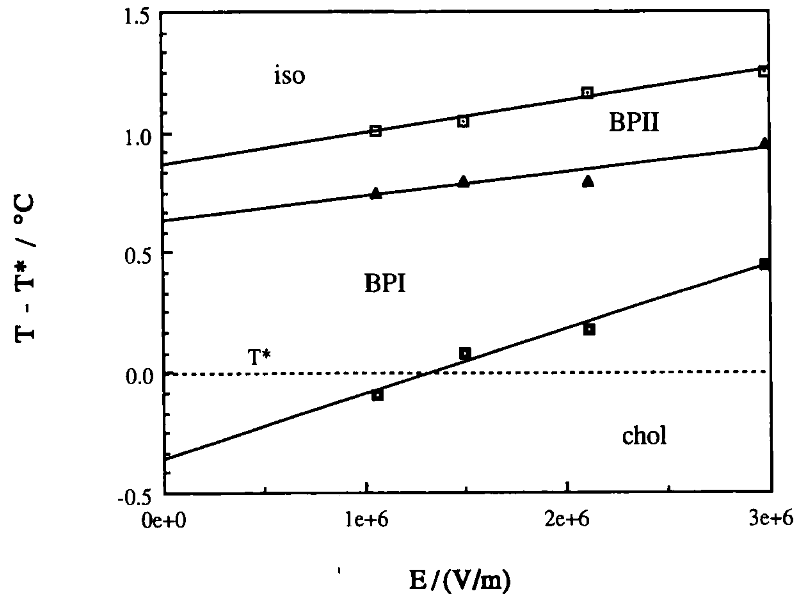

Figure 5. Temperature–electric field phase diagram for cholesteryl nonanoate.

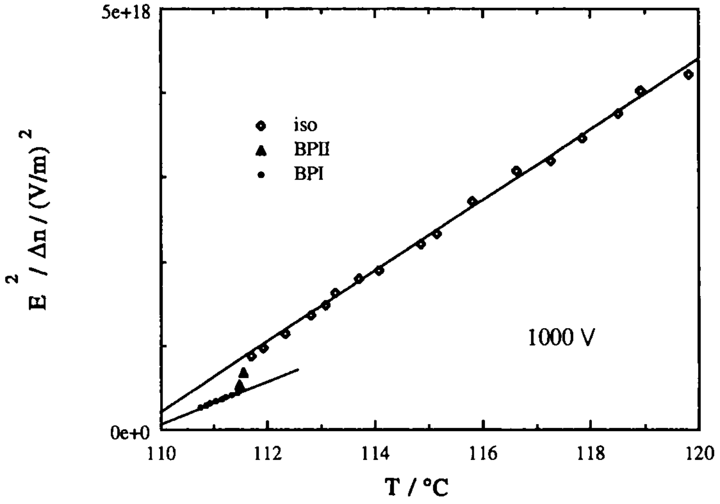

Figure 6. $E^2/\Delta n$ versus temperature for cholesteryl butyrate.

applied voltage. We see that behaviour is identical to that found for cholesteryl nonanoate except that the ranges of BP I and BP II are more abbreviated. In figure 7 are plotted the data for cholesteryl propionate. Here we see a discontinuity as we go directly from the isotropic phase to BP I, followed by the same type of linear behaviour within BP I as we have already discussed for cholesteryl nonanoate. Thus we see that the characteristic behaviour of the Kerr effect for the two blue phases is preserved in these homologues.

3.4. (+)-*2-methylbutyl-p-*[(*p-methoxybenzylidene*)*amino*] *cinnamate*

We have studied the compound (+)-2-methylbutyl-*p*-[(*p*-methoxybenzylidene)-amino] cinnamate (MBMBAC) primarily because it is a good example of a material

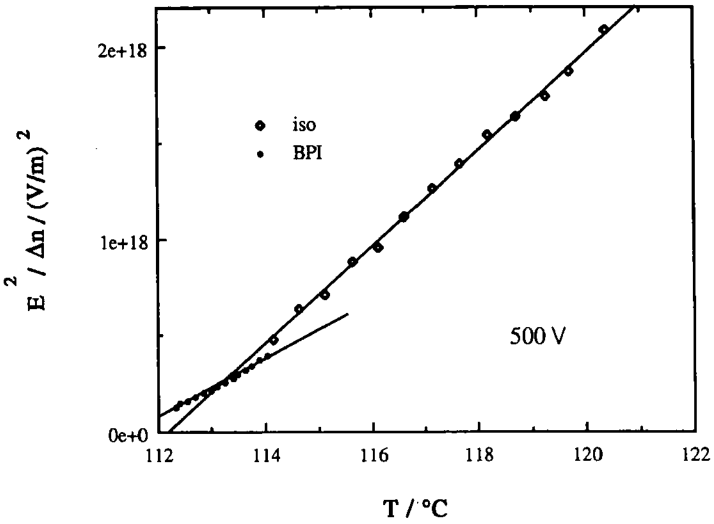

Figure 7. $E^2/\Delta n$ versus temperature for cholesteryl propionate.

having a BP III phase which is readily visible. Cholesteryl nonanoate is also reported to have a BP III existing over a range of about 0·2° [41], but this phase was not mentioned in our earlier discussion of this compound for the simple reason that it is not visible in our type of experiment, although optical rotatory [42] and calorimetric studies [41] clearly show its presence. In the case of MBMBAC, however, the BP III is easily seen as a uniformly grey and featureless form. Most likely the difference in our abilities to observe the BP III region in these two compounds is due to their large differences in optical anisotropies. The large anisotropy of MBMBAC also has bearing on the appearance of its other blue phases. In thin samples the BP I and BP II phases of MBMBAC look quite brilliant both in relected and transmitted light; a thin sample of CN, by way of contrast, is much less bright in reflected light and is almost invisible in transmitted light. In the thick samples of MBMBAC used in these experiments the BP I and BP II phases appear practically opaque in transmitted light because of this large dielectric anisotropy, and our results, therefore, for this compound are given only for the isotropic and BP III phases.

In figure 8 we display the data for an applied voltage of 140 V, corresponding to an electric field of only $4{\cdot}7 \times 10^5$ V/m. Here is another indication of the relatively higher dielectric anisotropy of MBMBAC compared to CN—the fields needed to produce similar amounts of birefringence are much smaller for MBMBAC. We also should note another difference, that the sign of the anisotropy is positive for MBMBAC whereas it is negative for the cholesteryl esters. Although the transition from the isotropic phase to BP III is visually quite apparent—the field of view suddenly becomes very foggy—there is little indication of a change in the birefringence measurements since the data continue the trend of the isotropic phase with only a slight departure from the linear behaviour. It is not so surprising, therefore, that the BP III region of CN was not detectable by this type of measurement either.

The range of BP III indicated in figure 8—about 0·6°—is significantly greatly than the range of about 0·1° that is observed in the absence of an applied field. Thus it appears that the electric field enhances the relative stability of the BP III phase, which

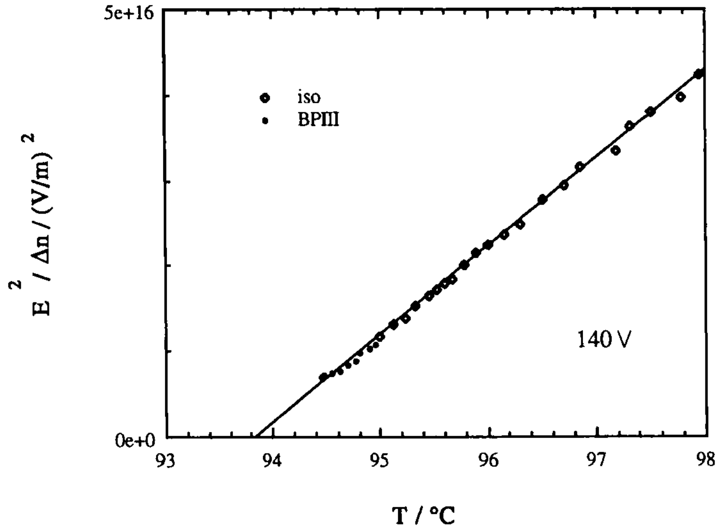

Figure 8. $E^2/\Delta n$ versus temperature for MBMBAC at an applied voltage of 140 V.

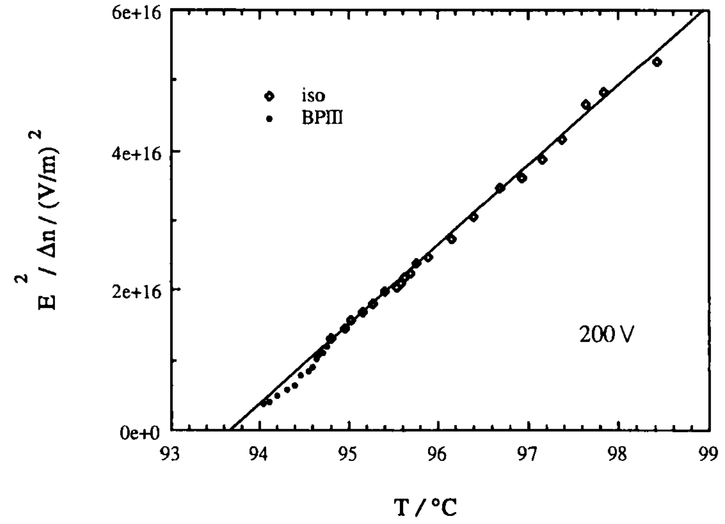

Figure 9. $E^2/\Delta n$ versus temperature for MBMBAC at an applied voltage over 200 V.

is the *opposite* of the behaviour found by Yang and Crooker [40], who, however, studied a material with *negative* anisotropy.

In figure 9 we show similar results obtained with a greater field. By comparison with the lower voltage data it is clear that the birefringence is again proportional to the square of the field, both in BP III and in the isotropic phase. The range of BP III is even more extended than with the lower voltage and, as it turns out, the extent of the BP I and BP II regions are correspondingly reduced. We know of no explanation as to why the behaviour of the BP III birefringence should be so similar to that of the isotropic phase or why the electric field should favour the BP III phase for a material of positive dielectric anisotropy. Perhaps these results will provide some important clues in unravelling the structure of this unusual phase.

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