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

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K. Pathmanathan [a b], L. A. Dissado [a] & R. M. Hill [a]
[a] The Dielectrics Group, Chelsea College, University of London, Pulton Place, London, SW6 5PR, U.K.
[b] Department of Metallurgy and Material Science, McMaster University, Hamilton, Ontario, K21 2M5, Canada
Version of record first published: 28 Mar 2007.

To cite this article: K. Pathmanathan , L. A. Dissado & R. M. Hill (1986): A Dielectric Study of the Solid Phases of M.B.B.A, Molecular Crystals and Liquid Crystals, 135:1-2, 65-91

To link to this article: http://dx.doi.org/10.1080/00268948608084806

Mol. Cryst. Liq. Cryst., 1986, Vol. 135, pp. 65–91
0026-8941/86/1352–0065/$25.00/0

Printed in the United States of America

A Dielectric Study of the Solid Phases of M.B.B.A.

K. PATHMANATHAN,† L. A. DISSADO and R. M. HILL‡

The Dielectrics Group, Chelsea College, University of London, Pulton Place, London SW6 5PR, U.K.

(*Received May 31, 1985; and in a modified form October 7, 1985*)

The effect of thermal history on the solid state phases of M.B.B.A. is investigated by examining the dielectric response of the solids formed by slow cooling the isotropic and nematic liquid crystals. In addition the relationship of these states to a glass is examined by studying the dielectric response of the quenched nematic liquid crystal.

Keywords: dielectric properties, MBBA, quenched mesophases

INTRODUCTION

Several investigations[1–5] have shown that solid N-(*p*-methoxybenzylidene)-*p'*-butylaniline (MBBA) can exist in at least three modifications depending upon its thermal history. In particular, a metastable crystalline state has been formed by slow cooling of either the nematic[4] or isotropic[5] liquid which converted[2,4] to the stable crystalline form only after standing at about 210 K for several hours, followed by heating to about 270 K. The relationships of the lattice structure of these states to the parent liquid crystal state and of their molecular motions to the phase transitions are still not completely resolved.[1,4,6] Because MBBA is a flexible polar molecule the molecular rearrangements in the solid may be studied through its dielectric response.[5,7–9] However a complete agreement between the different

†Now at Department of Metallurgy and Material Science, McMaster University, Hamilton, Ontario K21 2M5, Canada.

‡All correspondence should be sent to Professor R. M. Hill, Department of Physics, King's College (KQC), Pulton Place, London SW6 5PR, U.K.

investigators has not been obtained. We have attempted to clarify this situation by measuring, over a wider range of frequencies and temperatures than heretofore, the dielectric response of the solids formed by slow cooling the isotropic and nematic liquids.

The suggestion that a glassy nematic state can be formed by rapid cooling has also been investigated by measuring the dielectric response of the quenched nematic liquid crystal, and the results are compared with both the typical dielectric behaviour of glasses and of the slow-cooled nematic liquid.

EXPERIMENTAL

The dielectric cell was fabricated by cutting a circular hole of about 18 mm diameter in the centre of a 1 mm thick glass slide. A slot, 3 mm by 2 mm, was cut from one of the edges of the slide to the hole in order to fill the cell. Two similar microscope slides carrying evaporation deposited aluminium electrodes were glued to the first slide, with the conducting film inwards, to complete the cell. A syringe was used to fill the cell, using liquid MBBA at the desired temperature, but the filling slot was left free in order to allow for expansion. Only 0.25 cc of liquid was required to fill the cell and this low thermal mass ensured that the sample could be rapidly brought to any desired temperature.

The dielectric capacitance was measured in the frequency range from 10^{-2} Hz to 10^{5} Hz by means of a Frequency Response Analyser[10] (FRA) and a General Radio Bridge. The capacitance of the empty cell was about 2 pF and its temperature dependence due to thermal expansion/contraction was negligibly small ($<< 10^{-4}$/K). Because the capacitance measurements could be made more accurately than the size of the cell could be measured all the data will be reported here in terms of capacitance and loss, the latter being given by the conductance divided by the radian frequency. For the plane parallel cell used here $C = \epsilon_o \epsilon_r A/d$, where the symbols have their conventional meaning, and $\epsilon_r = \chi + \epsilon(\infty)$ where χ is the susceptibility.

RESULTS

Two different types of experimental practice have been adopted in this investigation. The first of these was used as a preliminary examination and consisted of measuring at a chosen fixed frequency during a cooling/heating cycle at 1K/min., with a waiting period of 45 minutes at the lowest temperature, that of liquid nitrogen. In the case of the quenched nematic liquid only the heating part of the cycle

could be measured in this way. The second stage of measurement involved the preparation of the system at liquid nitrogen temperature, as before, followed by heating to the desired measuring temperature. The dielectric response was then measured as a function of frequency over the frequency range, a process which required between half an hour and one hour at each temperature.

A. Slow cooled isotropic liquid crystal

The sample was heated slowly to 328 K and left for thirty minutes to bring it to the isotropic state before being subjected to the cooling/heating cycle. The capacitance and loss measured at 1.78 kHz during the cycle are shown in Figures 1(a) and (b), respectively. The most obvious feature of Figure 1(a) is the supercooling of the liquid state to 265 K, at which temperature a discontinuous change in the capacitance occurs which is accompanied by a similar discontinuity in the loss, Figure 1(b). It is apparent from a comparison of the loss curves from the cooling and heating cycles in the temperature range 240 K to 297 K, that the supercooling lies in the region of a large dielectric dispersion which is responsible for the lack of sharpness observed at the melting transition. Melting is completed by 297 K and the original liquid response is fully recovered.

A number of dielectric relaxations can be seen in both heating and cooling curves at lower temperatures, with the most prominent peak in the region of 200 K being that studied previously.[5,7-9] These processes are most conveniently examined at constant temperature, thereby avoiding any problems of temperature lag. The dielectric response obtained in this way is shown in Figure 2. Here data covering the temperature range 113 K to 213 K has been normalised by translating the observed response measurements along the logarithmic amplitude and frequency axes so that their curvature in the region of the peak is contiguous.[11] The frequency dependence of the loss peak has been described by means of the theoretical susceptibility function[12,13]

$$\chi'(\omega) - i\chi''(\omega) = \chi(0)\, F(\omega/\omega_p) \tag{1}$$

with

$$F(\omega/\omega_p) = F_o(1 + i\omega/\omega_p)^{n-1} \cdot {}_2F_1\left(1 - n, 1 - m; 2 - n; \frac{1}{1 + i\omega/\omega_p}\right) \tag{2}$$

where F_o is a numerical normalising function such that $F(0)$ is unity,

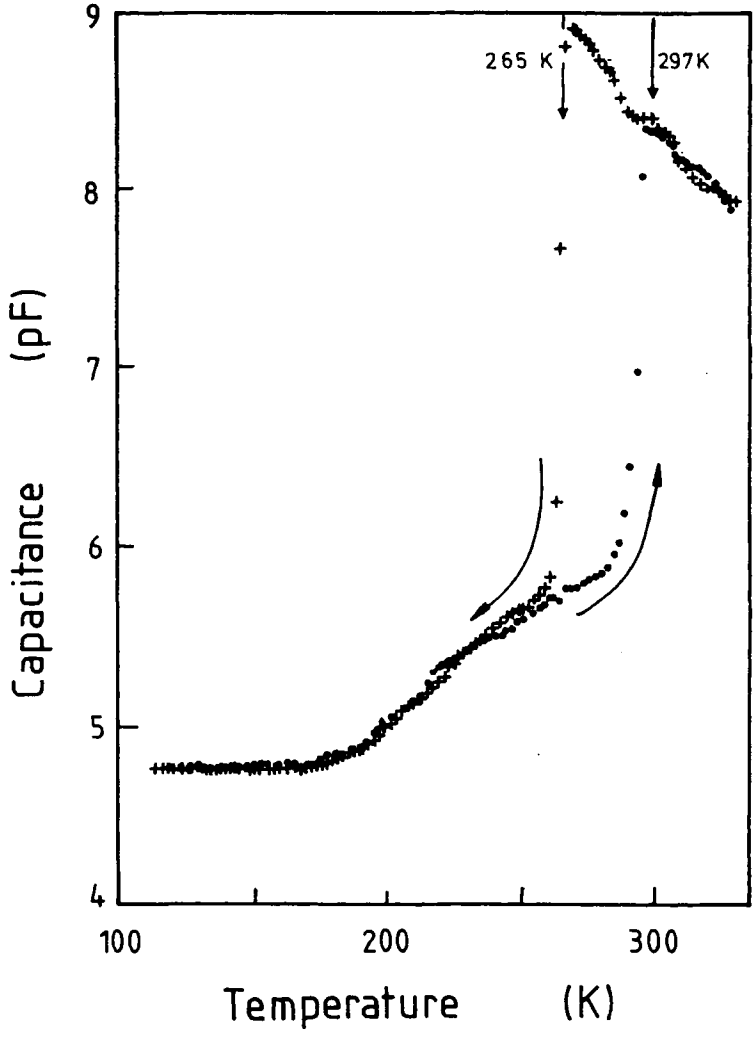

FIGURE 1 (a) The dielectric response at 1.78 kHz of the isotropic liquid during slow cooling and then re-heating. Diagram (a) shows the capacitance on a linear scale and diagram (b) the dielectric loss on a logarithmic scale.

ω is the circular frequency, ω_p the characteristic relaxation rate and ${}_2F_1(,;;)$ the hypergeometric function.[14] The susceptibility function of equation (1) has the asymptotic limits

$$\chi'(\omega) \propto \chi''(\omega) \propto (\omega/\omega_p)^{n-1} \quad , \quad \omega >> \omega_p \qquad (3a)$$

$$\chi''(\omega) \propto \chi'(0) - \chi'(\omega) \propto (\omega/\omega_p)^{m} \quad , \quad \omega << \omega_p \qquad (3b)$$

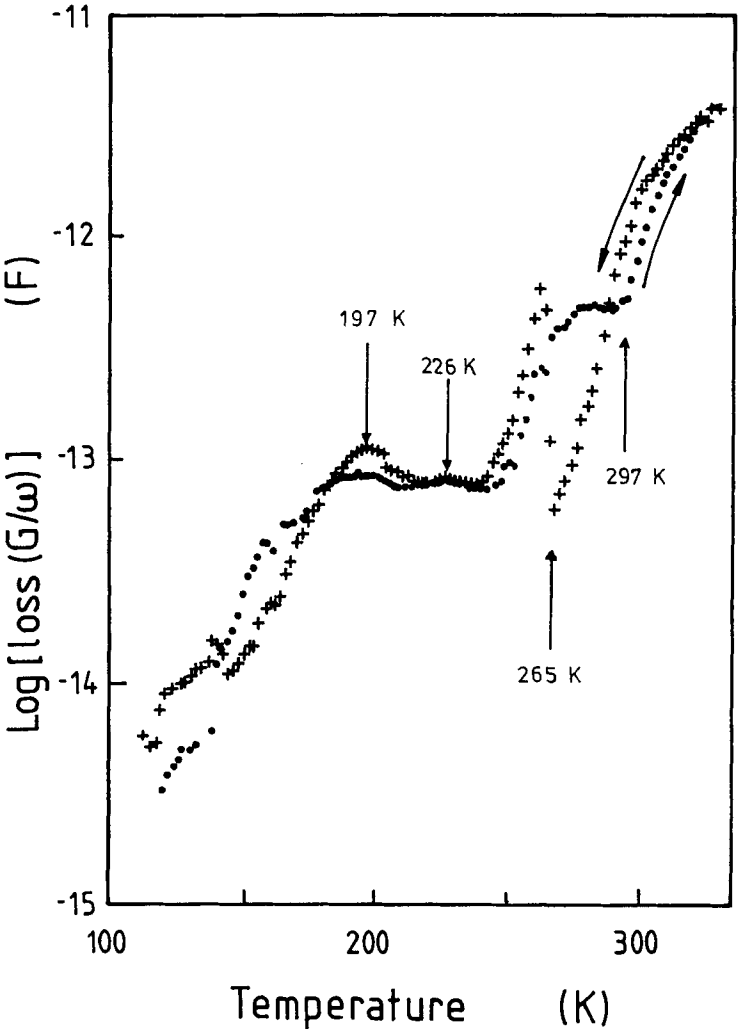

FIGURE 1 (b) *Continued*

with $$0 < n,m < 1 \quad (4)$$

and has been shown to apply with complete generality to all shapes of dielectric loss peaks.[15]

The loss peak shown in Figure 2 changes shape slightly up to 153 K and thereafter remains invariant over the measured temperature range up to 228 K. The theoretical function presented for comparison in Figure 2 has been fitted to the high temperature range. At low fre-

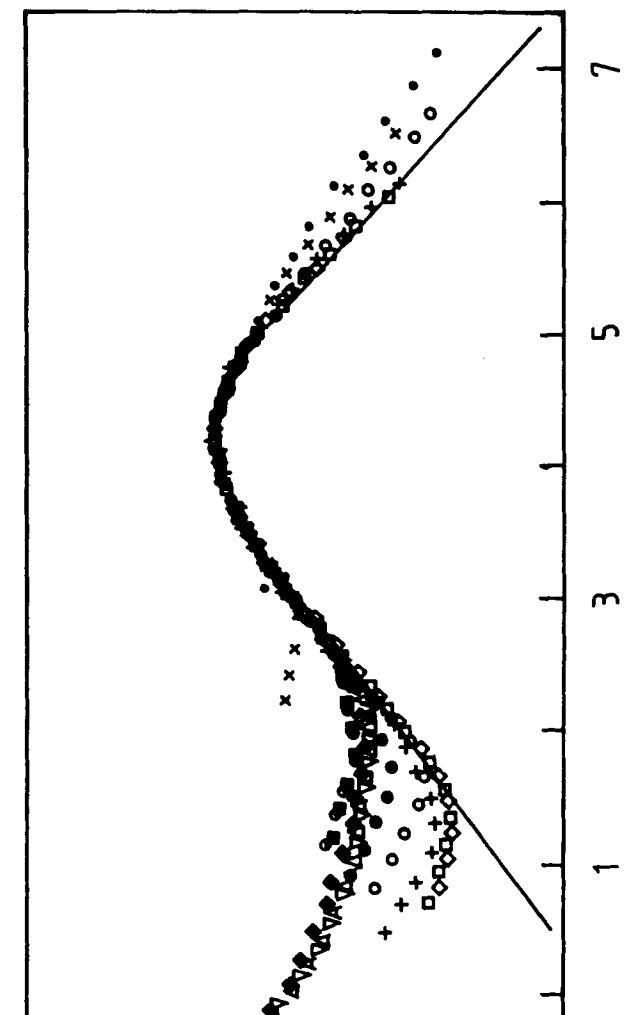

FIGURE 2 The dielectric response of the slow cooled isotropic solid, case A, in the temperature range 133 K to 228 K. The plot is scaled at 203 K, at which temperature the scales are absolute, and the experimental data has been normalised on the peak loss. The curve through the data points is theoretical and has been obtained from equation (2) with $m = 0.39$, $n = 0.56$, $\chi(0) = 8.2\ 10^{-13}$ F, and a peak loss frequency of $1.6\ 10^{4}$ Hz, these latter two values being absolute for the scaling temperature.

● 133 K, × 143 K, ○ 153 K, + 163 K, □ 173 K, ◇ 183 K, ● 193 K, △ 198 K, ▽ 203 K, ◆ 208 K, ■ 213 K and ◒ 228 K.

quencies the same diagram shows the rising tail of the loss process which can be seen as beginning at 240 K in Figure 1(b). In addition a weak loss mechanism appears briefly at intermediate frequencies in the range 198 K to 213 K and disappears by 228 K. This can be seen as the weak maximum around 225 K in Figure 1(b).

B. Slow cooled nematic liquid crystal

The initial state for this sample was the nematic liquid crystal at room temperature and the dielectric response measured at 1.78 kHz during the cooling/heating cycle is given in Figures 3(a) and (b). It is noticeable that the capacitance of the initial liquid crystal lies midway in the discontinuity attributable to the melting of the solid, which is only completed by 303 K. There is no obvious evidence of supercooling. These factors imply that crystallisation from the nematic liquid is extremely rapid when compared with the equivalent behaviour of the isotropic liquid. A second point of difference between this and the previous case, A, is in the behaviour of the capacitance after the solid has melted, which is almost temperature independent unlike that shown in Figure 1(a). There is certainly no major change marking the nematic/isotropic transition, which was expected to occur in the region of 317 to 319 K.[4] The difference in the nematic liquid response following melting, between this case and case A may be due to different director configurations in the original liquid. In case B, these random alignments may be eliminated during temperature cycling. However in case A they are likely to be preserved, since the large supercooling would be consistent with the formation of many crystalline regions based on the original director alignments. However, one feature in common with case A is the existence of a large dielectric dispersion, starting at 260 K, which is intercepted by the melting transition before a peak can be reached.

Below 260 K two major dispersions exist lying between 208 K and 250 K, and 127 K and 200 K, at this frequency. It is the lower of these that has been investigated by means of constant temperature measurements. The results are shown in Figure 4(a) and (b) where the theoretical function, equation (2), has been fitted to the loss peak. Although there is a change in shape in the region of 155 K to 165 K no further changes were observed up to a maximum measurement temperature of 221 K, as can be seen in Figure 4(b). In these figures the second loss process appears only as a rising tail at low frequencies which increases slightly in prominence between 183 K and 193 K.

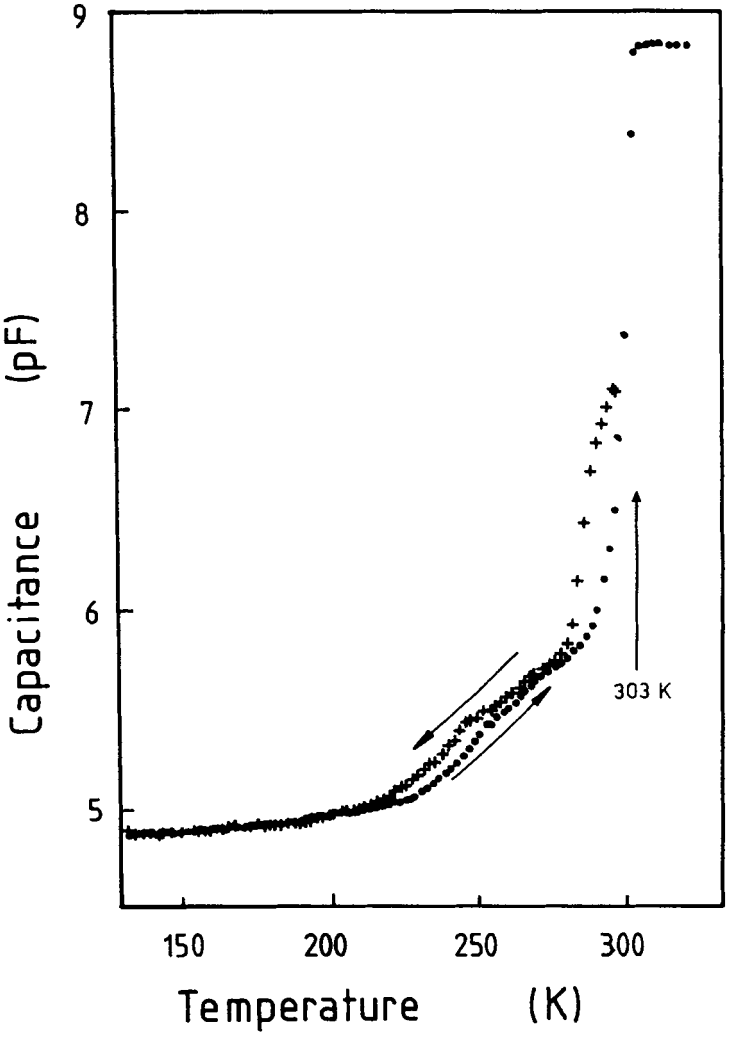

FIGURE 3 (a) The dielectric response of the nematic liquid during slow cooling from the nematic state and re-heating into the isotropic liquid state. The frequency of measurement was 1.78 kHz. Diagram (a) shows the capacitance and diagram (b) the loss.

C. Quenched nematic liquid crystal

The nematic liquid crystal at room temperature was quenched rapidly to liquid nitrogen temperature, this temperature being achieved in 5 to 10 minutes. After waiting for forty-five minutes the dielectric response at 1.78 kHz was measured while heating at the rate of

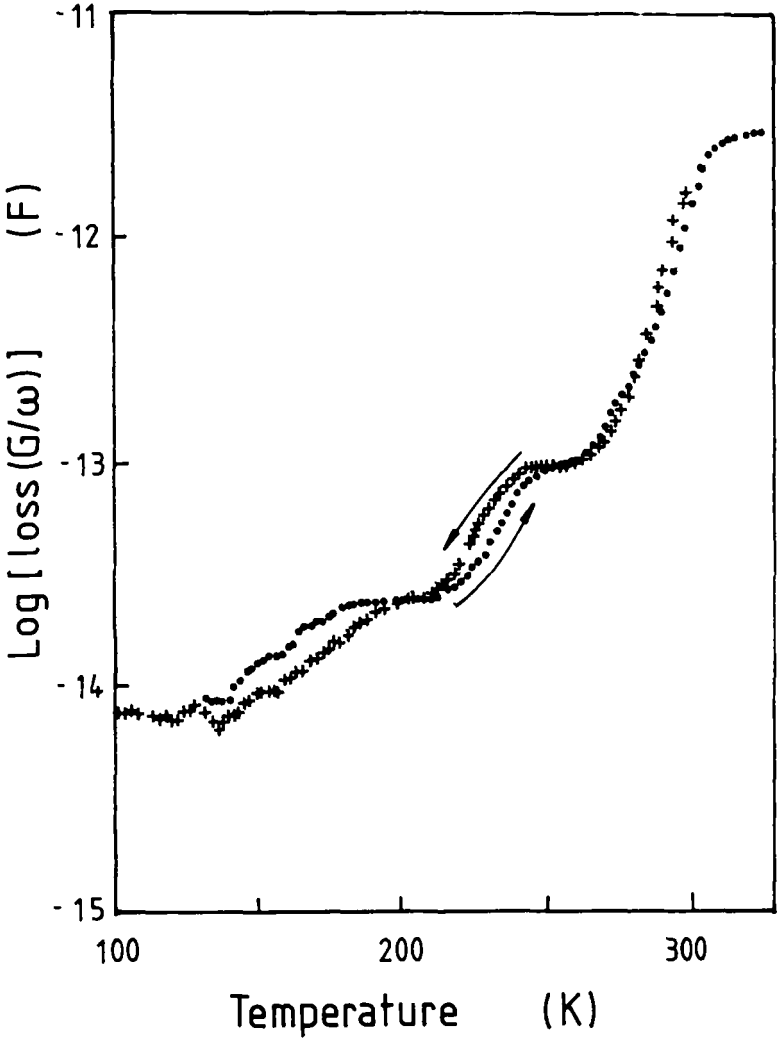

FIGURE 3 (b) *Continued*

1K/min., and is shown in Figure 5. These measurements show two major features; a loss peak centered around 215 K and a discontinuity in capacitance at the melting point. The behaviour of the loss peak in showing a sharp discontinuity at 298 K indicates that the capacitance dispersion between 260 K and 298 K should be attributed to a dielectric dispersion in the solid which is interrupted by melting, just as in both previous cases. The temperature dependence of the ca-

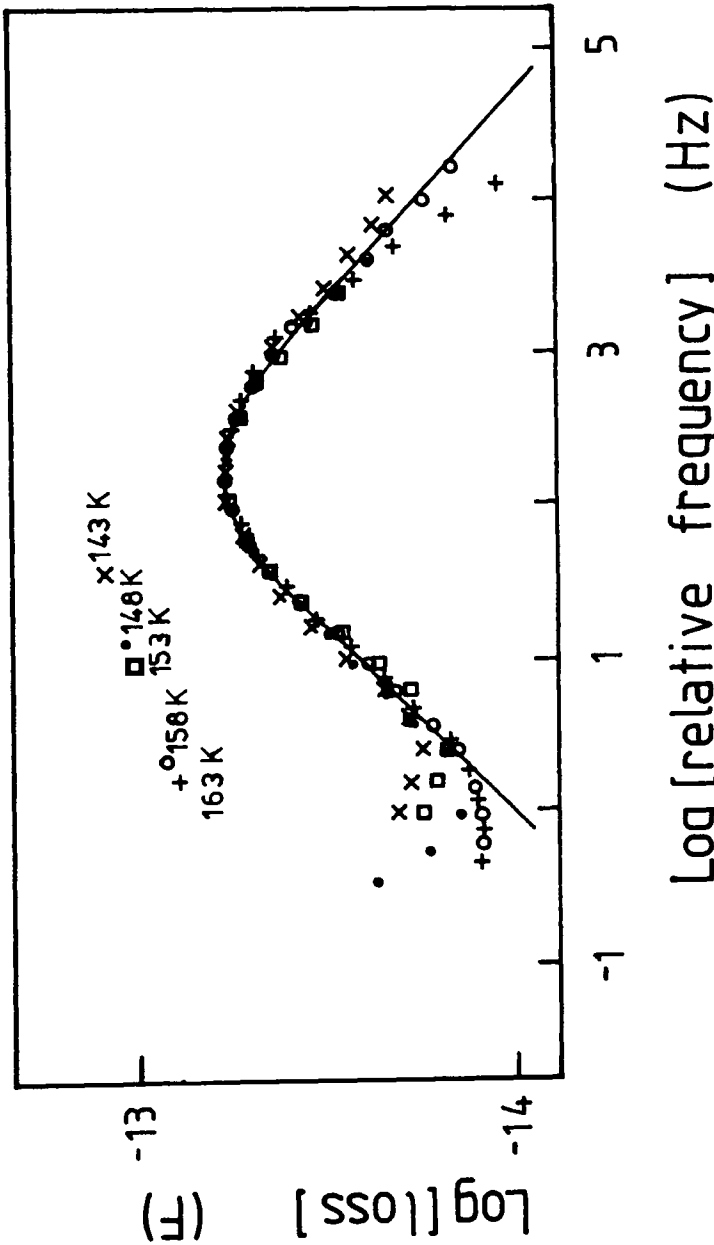

FIGURE 4 The dielectric response for the slow cooled nematic, case B, in the temperature range 143 K to 220.5 K.

(a) Spectra for the temperature range 143 K to 163 K in a normalised plot scaled at 153 K. The normalisation shift points are shown in the upper part of the diagram and give the key to the symbols. The theoretical shape curve has been obtained from equation (2) with $m = 0.45$, $n = 0.60$, $\omega_p = 1.5\ 10^2$ Hz and $\chi(0) = 2.7\ 10^{-13}$ F.

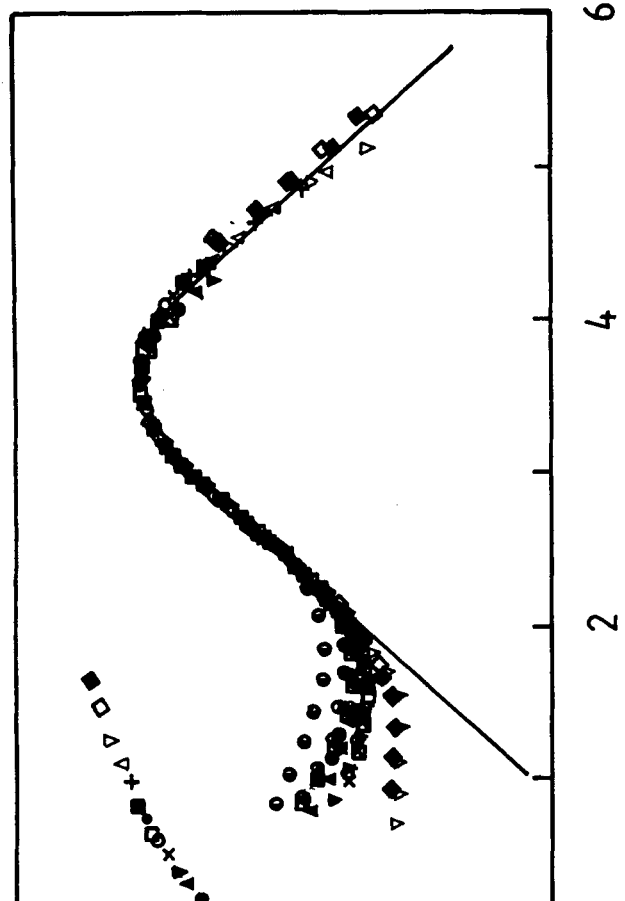

FIGURE 4 *Continued*
(b) Spectra for the temperature range 168 K to 220.5 K, normalised at 188 K. The theoretical shape curve of equation (2) with $m = 0.45$, $n = 0.53$, $\omega_p = 4.6\ 10^3$ Hz and $\chi(0) = 3.3\ 10^{-13}$ F is also shown.
◆ 168 K, ◇ 173 K, ▽ 178 K, △ 183 K, + 188 K, ■ 193 K, ● 198 K, □ 200.5 K, ○ 203 K, × 205.5 K, ▼ 208 K, ▲ 210.5 K, ● 213 K, □ 215.5 K, ◐ 218 K, and ◐ 230.5 K.

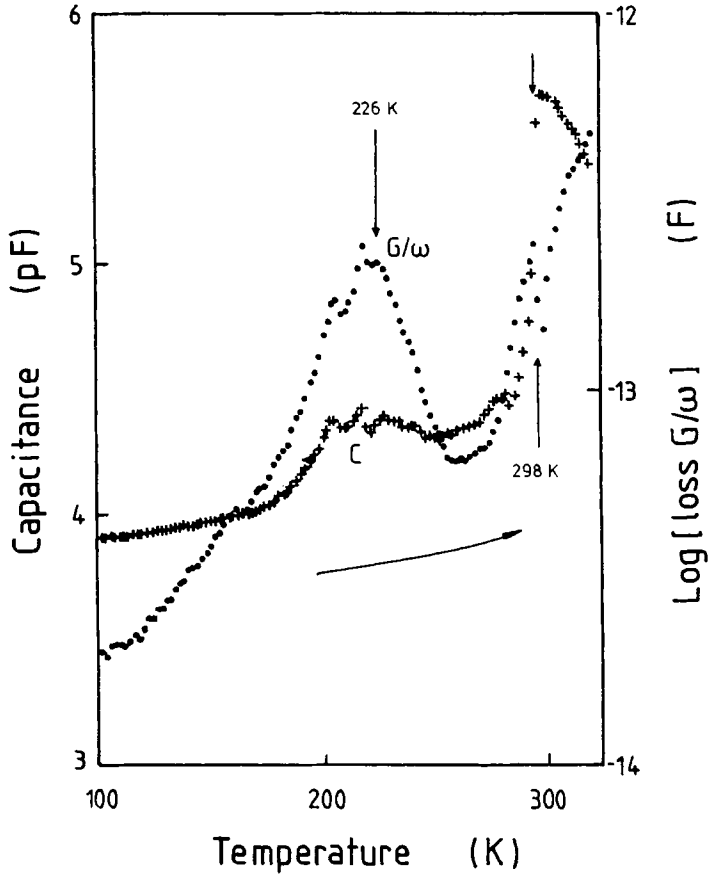

FIGURE 5 The dielectric response at 1.78 kHz of the rapidly cooled glassy material as it was heated from the quenching temperature.

pacitance following melting has the form exhibited by case A rather than that of case B, and thus it seems that during this thermal run the system has not lost all memory of the original state.

Although the main peak at 215 K shows fine structure at 200 K and 216 K associated with minor discontinuities in capacitance, there is no sign of the separate broad low temperature peak usually accepted as one of the dielectric signatures of a glassy material.[16] This region of response has been investigated in more detail through the constant temperature measurements presented in Figures 6(a) to (c). It is observed that the principal peak is broad at low temperatures and suffers some minor shape changes before undergoing a major sharpening at 200 K, thereafter remaining unaltered. It is however, the

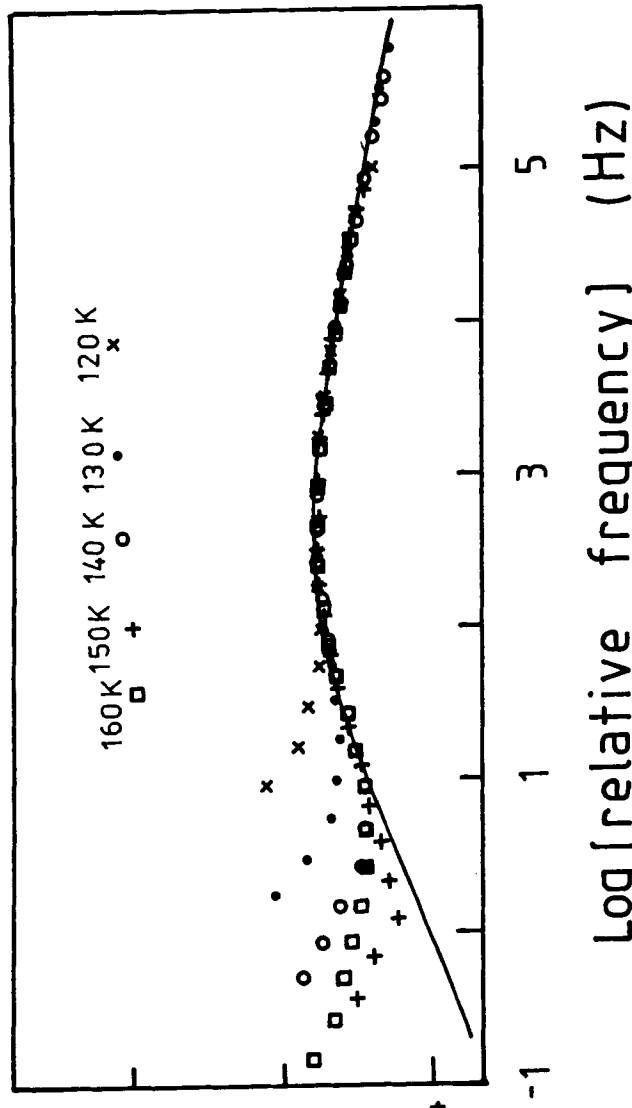

FIGURE 6 The dielectric response of the quenched nematic, case C.

(a) Spectra for the temperature range 120 K to 160 K, normalised at 150 K. The theoretical curve was obtained with $m = 0.40$, $n = 0.82$, $\omega_p = 1.2\ 10^2$ Hz and $\chi(0) = 4.0\ 10^{-13}$ F.

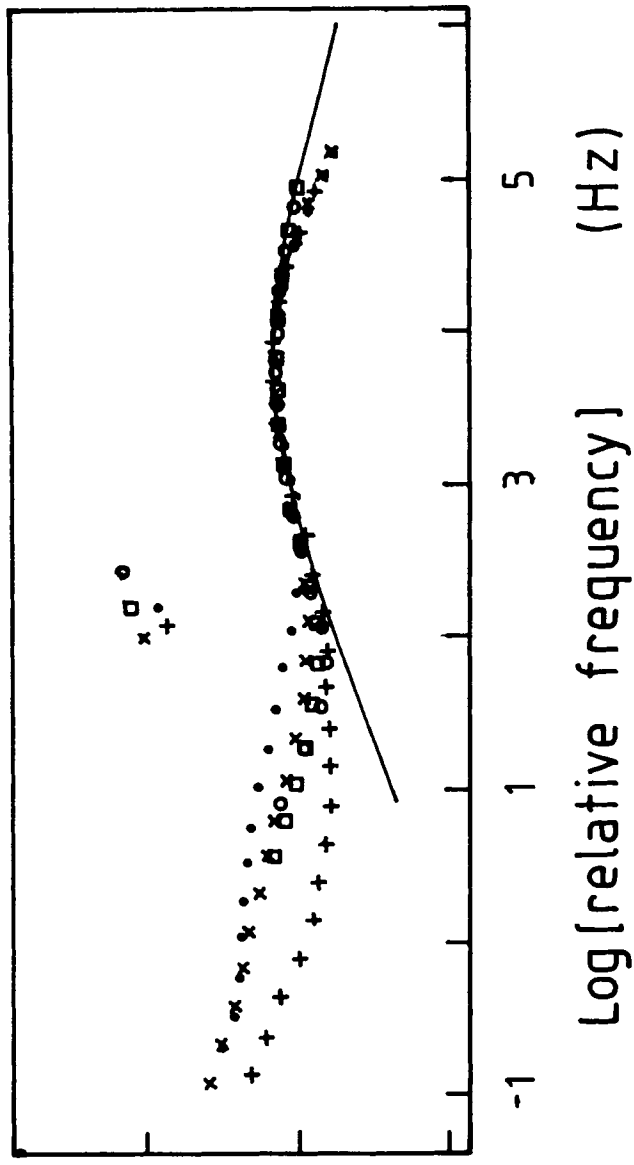

FIGURE 6 *Continued*

(b) Spectra for the temperature range 170 K to 195 K together with the theoretical shape function with $m = 0.35$ and $n = 0.75$. At the plot normalisation temperature, 180 K, $\chi(0) = 6.5\ 10^{-13}$ F and $\omega_p = 4.2\ 10^3$ Hz.

○ 170 K, □ 175 K, × 180 K, ● 190 K and + 195 K.

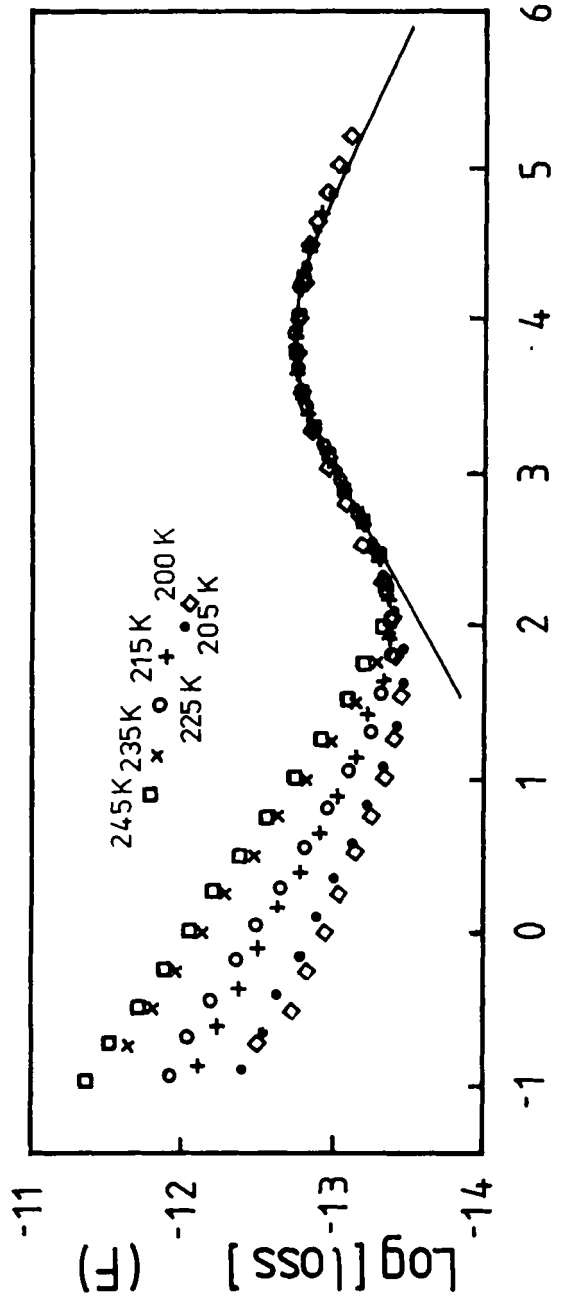

FIGURE 6 *Continued*

(c) Spectra for the temperature range 200 K to 245 K, normalised at 205 K, together with the theoretical shape function of equation (2) for $m = 0.50$, $n = 0.50$, $\omega_p = 9.7\ 10^3$ Hz and $\chi(0) = 7.3\ 10^{-13}$ F.

same peak that is observed throughout rather than a different relaxation mechanism which moves into the frequency window of investigation. In the temperature range between 180 K and 195 K, a weak subsidiary loss peak is also observed, lying to lower frequencies than that of the main peak. Above 195 K this weak peak disappears rather than moves out of the frequency range. This is similar to a feature observed in case A in the slightly higher temperature range of 198 K to 213 K. Since the subsidiary maximum has no observable contribution above 200 K it appears that the fine structure in Figure 5 should be attributed to the shape changes. The other feature of Figure 6(c) is the presence at lower frequencies, of the rising tail of the strong dispersion observed in Figure 5 above 250 K.

DISCUSSION

The sum total of the information that can be obtained from dielectric studies is contained in the dependence upon the controlled variables of the loss peak shape, given in this case by the values of the indices n and m; the dielectric dispersion in capacitance, proportional to $\chi(0)$; and the relaxation rate, ω_p. These are shown as functions of temperature in Figures 7 to 9. The Arrhenius form has been used for the presentation of the rate rather than the Eyring expression used by Yasuda *et al.*,[9] because the latter expression applies when the dipole has an unbound motion along the relaxation coordinate outside of the activated state. The assumption made by Yasuda *et al.* cannot be justified on an *a-priori* basis in a solid, and since the temperature necessary to demonstrate the existence of a kT/h prefactor is not accessible in this state, the Arrhenius plot should be used.

General

Some general points can be made immediately. The differences in amplitude, spectral shape and relaxation rate between the slow cooled isotropic and nematic liquid crystals indicate some differences in these solid states. This conclusion is substantiated by the differences in the dielectric behaviour of the two systems after melting. However a comparison with the results reported by Moscicki[5] shows that neither of these states can be identified as the stable crystal state. Thus both states must be regarded as metastable with the slow cooled isotropic liquid, case A, being the one previously studied, as shown in Figure 10 which compares the present relaxation rates with those of earlier workers.

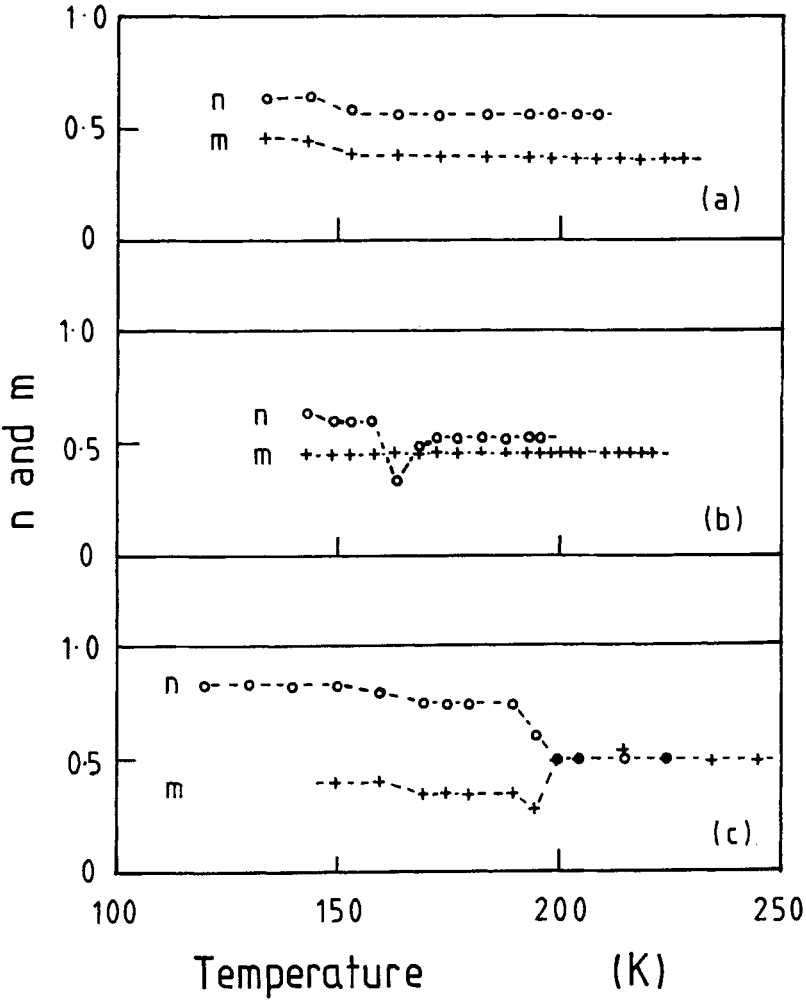

FIGURE 7 Variation of the shape parameters m and n with temperature.
(a) Metastable solid from the slow cooled isotropic liquid crystal, case A.
(b) Metastable solid from the slow cooled nematic liquid crystal, case B.
(c) Solid formed by the quenched nematic liquid crystal, case C.

A second general point is that the activation plot of the quenched nematic crystal shows no sign of the characteristic slowing down of the relaxation rate of an α-branch as the glass transition is approached in a typical glass.[16] Indeed Figure 9 shows that except for the quenched material at low temperatures the relaxation rates of all systems have

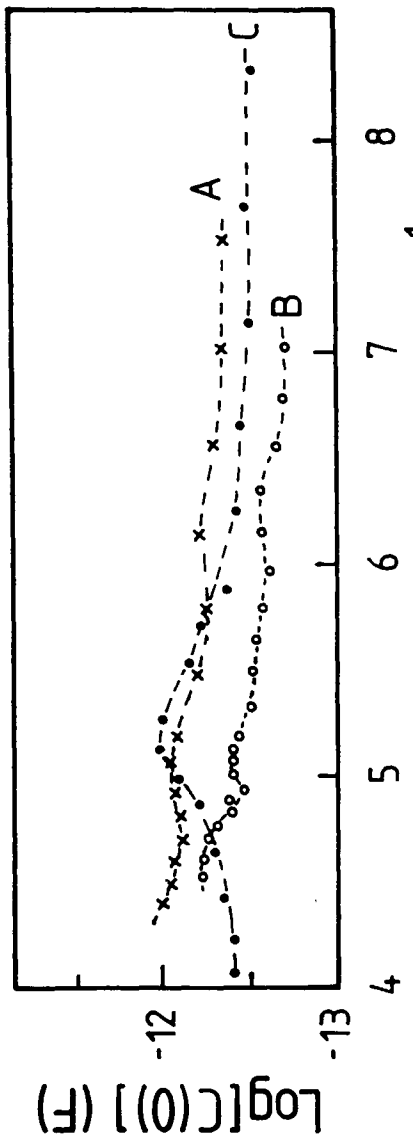

FIGURE 8 Variation of the dielectric dispersion $\chi(0)$ with temperature for the three cases which have been examined.

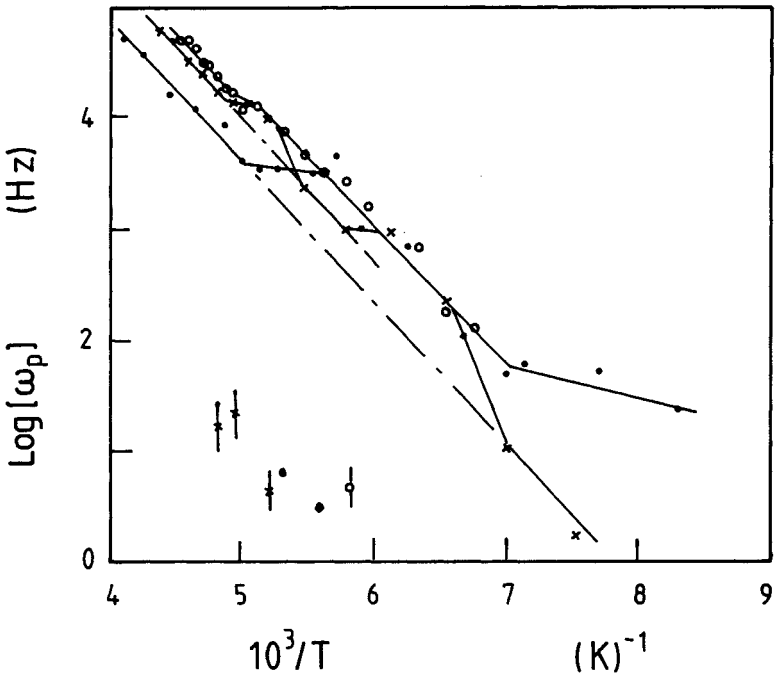

FIGURE 9 Arrhenius plots of the relaxation rates for the three cases. The lines through the points have been added to aid the eye in following the changes in behaviour. × Case A, ○ Case B and • Case C.

effectively the same activation energy, about 0.25 eV (5.8 Kcal/mole), differing only in their pre-exponential factors. This value of activation energy (which has been obtained as a general trend over a wider range of temperature than has previously been measured) is at the low end of the range quoted,[5,7–9] and has been attributed variously to temperatures below 200 K[8] and above 200 K.[7] It has been implied by Agarwal[8] that the loss process observed in case A could be regarded as an ($\alpha\beta$) peak such as may be found at temperatures greatly in excess of the glass transition temperature in polymers,[17] in which case high pressures can be used to resolve the two processes.[17] Yasuda *et al.*[9] have shown that although the application of pressure shifts the loss maximum in the *metastable* solid, case A, the peak is not split into two. Thus at least in the metastable cases (A) and (B) the loss peak must be taken to refer to a single mechanism, and these structures cannot be regarded as glassy in a dielectric sense.

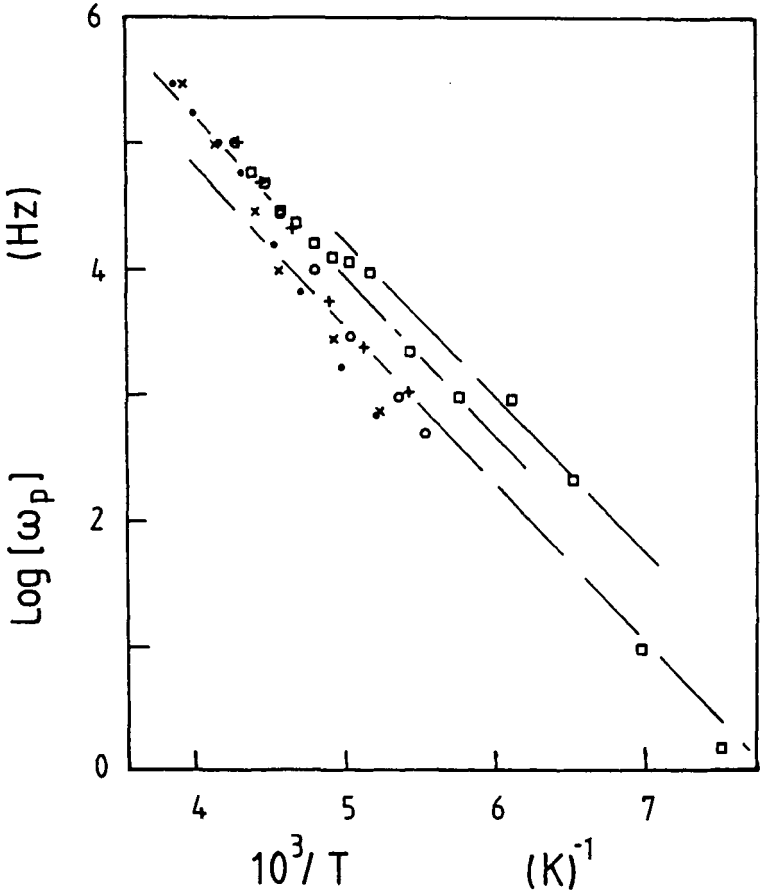

FIGURE 10 Comparison of the Arrhenius plots of the slow cooled isotropic liquid, case A, with data reported by other workers. The lines shown in this plot are taken from the activation plot shown in Figure 9.

× Moscicki,[5] ● Moscicki and Urban,[7] + Agarwal *et al.*,[8] ○ Yasuda *et al.*,[9] □ this work.

Activation entropy

The difference between the various sections of the Arrhenius plot for the range of samples indicated in Figure 9 lies in different values of the activation entropy ΔS^* since

$$\omega_p = \nu_o \, e^{\Delta S^*/k} \, e^{-\Delta U^*/kT} \tag{5}$$

However the direct comparison of our results with those of Yasuda

et al.[9] is not easy because the pre-factor depends crucially on the activation energy chosen for extrapolation. Thus although the previously reported relaxation rates lie close to those obtained here, as shown in Figure 10, there are considerable differences between the pre-exponential values due to the larger activation energies that have been used. Nevertheless, if we take account of the arbitrarily introduced pre-factor of kT/h of Yasuda *et al.*[9] (which varies only between $2\ 10^{11}$ and $6.25\ 10^{11}$ in the temperature range 100 K to 300 K) we find that all our loss mechanisms have negative activation entropies, in contrast to those determined by Yasuda *et al.* We note, however, that a negative value of ΔS^* would arise even with Yasuda's data if ν_o were taken as a lattice vibration frequency. This observation implies that the ground state of a relaxing centre possesses sufficient free volume to allow it to adopt specific configurations which lead to a minimum barrier for re-orientation, and would be consistent with the observed increase in ΔS^* with pressure.[9] Under these circumstances the ground state free volume[18] would be reduced so that eventually a centre would have to generate free volume in order to relax and ΔS^* would be positive and ΔU^* higher. Such considerations lead to the conclusion that (with the exception of the glass below 143 K) all the systems studied here possess centres with dipoles which relax by adopting specific configurations to cross the *same* potential barrier. The different pre-exponential factors arise from differences in the free volume of the ground state in the various cases.

Spectral response

Differences in the free volume of the relaxing centre are likely to account for the observed changes in spectral shape which have been quantified on the basis of the theoretical model that gives the shape function of equation (2). The relaxing centre is regarded as a cooperatively displacing group comprising the dipoles and their environment.[13,19] Relaxation then proceeds by the progressive displacement of increasingly larger sub-units up to the size of the centre, with the index n defining the self-similarity[20] between different size sub-units. Thus $n \rightarrow 1$ indicates a centre where a re-orientable dipole forms part of a near rigid lattice structure, whereas $n \rightarrow 0$ applies to a dipole which is enclosed within a nearly undeformable cage. In the former case motion of the dipole is strongly coupled to the lattice structure and in the latter case the structure is minimally affected by re-orientation of the dipole. The index m describes the way in which non-dipolar structural fluctuations at one centre can influence another

relaxing centre. The Glarum[21] 'defect' diffusion could be regarded as a specific form of this mechanism with limited applicability. In general a value of m approaching unity indicates a large number of small independent displacements in the environment of the centre. This may occur when the reorientation of a dipole causes changes in position of a large number of nearly free non-polar side groups, the disturbance produced is transferred through steric interactions causing small adjustments of dipole orientations at other molecules. When dipole re-orientations cause few but large reorganisations of the non-polar side groups, such as may be the case in tangles or glassy molecular structures, the transmitted disturbance causes considerable reorientation at other dipole sites and m approaches zero.

The shape indices plotted in Figure 7 show that case A, below 150 K, and case B, below 135 K, have similar shapes. However the self-similarity index n changes discontinuously for case B between 150 K and 170 K, indicating a spontaneous reduction in the dilation (self-similarity in scale) symmetry of the centre, which may also be associated with the change in activation entropy observed around this temperature. Case A, on the other hand, shows only a small reduction which is insufficient to materially affect ΔS^*. The quenched material however shows a number of small changes although the shape remains typical of that of a broad β peak up to 200 K. This indicates a structure which is close to ideal self-similarity, and thus local rigidity. Above 200 K the change in shape implies that the local self-similarity is considerably reduced and the influence of non-dipolar environmental fluctuations somewhat increased. It can be seen that for temperatures above 200 K the shape of the loss peak is almost, but not completely, symmetrical ($m + n = 1$) as has been assumed by other workers[8,9] and does not have the Cole-Davidson form ($m = 1$) as reported by Moscicki and Urban.[7] This may be one reason for reports of shape changes at this temperature, since curve fitting to the symmetric function will lead to a variation in the fitted shape as the high frequency side of the peak gives way to the low frequency side in the frequency window. As an illustration we show in Figure 11 the loss peak at 4kbar pressure extracted from the data of reference 9, and note that n is slightly increased from the value reported here whereas m is substantially increased, as might be expected from the local and long range structural effects that determine these parameters. The change in Cole-Cole parameter quoted in reference 9 ($0.62 \rightarrow 0.4$) therefore must be associated, mainly, with the change in assymetry.

On the basis of the above considerations it appears that the shape changes observed here should be ascribed to local and long-range

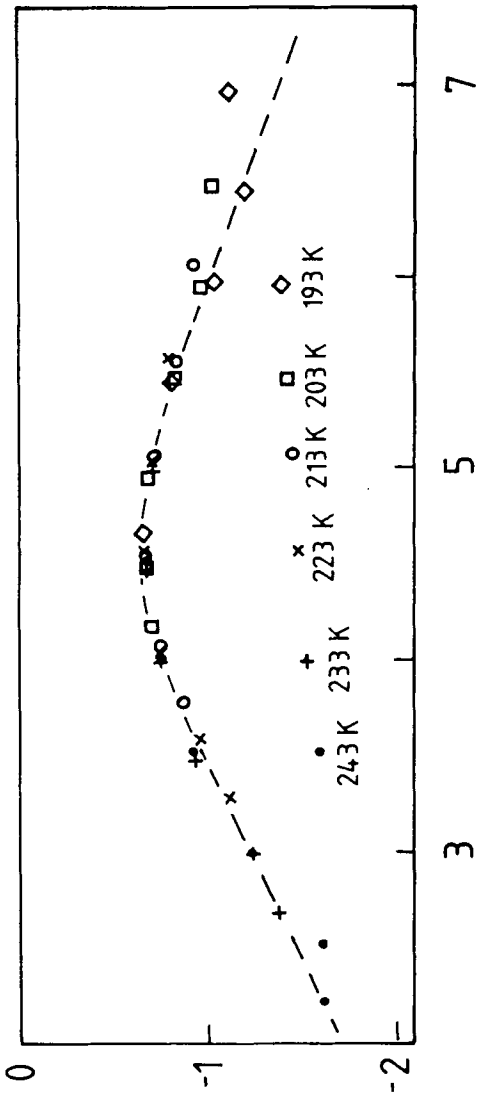

FIGURE 11 The dielectric response of the metastable state (case A) at 4 kb pressure as reported by Yasuda *et al.*[9] The plot has been normalised with respect to temperature and is scaled at 233 K. The theoretical function of equation (2) has been superimposed with $m = 0.50$ and $n = 0.63$.

structural reorganisations as the system expands, which is therefore not a continuous isotropic process. In view of some differences between our results and those of other workers it may be of significance that our cell was open and allowed expansion, a feature which may not have been possible with other cell geometries.

The region of the specific heat anomaly

Much of the interest in the solid MBBA system is concentrated upon determining what changes occur in the region of 200 to 225 K to give the observed specific heat anomaly,[2] and prepare the metastable solid for 'spontaneous' transition[4] to the stable crystalline state around 270 K. In all the systems studied here this region is marked by a peak in the dielectric dispersion, Figure 8, which confirms the result of Agarwal *et al.*,[8] and shows that the re-orientable dipoles are affected by this change. However unlike Agarwal *et al.* no spectral shape change has been observed at this temperature, except in the case of the quenched material. Furthermore the activation plot of the relaxation rate shows at most a kink at this temperature rather than the distinct change in activation energy which has been suggested.[8] This result is in agreement with the findings of Yasuda *et al.*[9] at atmospheric pressure, where a kink can also be noted. It can be concluded on the basis of these observations that in cases A and B the observed relaxation must be attributable to dipoles which are reorientable both above and *below* the crucial temperature region, although a peak in their number density is found there. However the appearance of a weak subsidiary loss peak around this temperature in both cases A and C may be attributable to dipolar groups which only become reorientable in the temperature range between 190 K and 220 K. In this case their considerably lower relaxation rates indicate a different local environment to that of the major relaxing centres. Andrews[6] has suggested that the sharp specific heat anomaly at 217 K is due to an order/disorder transition of the methoxy dipole, and the broader peak to the melting of the butyl end chain conformations. However the peak in $\chi(0)$ for case A and case B, Figure 8, are approximately 0.5 and 0.2, respectively, which represent 0.36 and 0.15 of the dipole strength of the methoxy dipole.[9] These values are consistent with the previous estimates[7,9] at this temperature and indicate that the main peak arises from the methoxy dipole which is reorientable at all temperatures, and hence Andrews[6] suggestion cannot be substantiated. On the other hand Arendt *et al.*[1] have shown that the benzylideneaniline core, which in the quenched nematic is frozen in

random orientations, has two alternative configurations in the metastable state. Thus it seems likely that the peak in dispersion in case C in the region of 190 K is due to the effect of the unfreezing of the benzylideneaniline core upon the methoxy dipole which will be reorientable at this temperature. In which case the maximum in $\chi(0)$ for cases A and B probably refer to the effect upon the methoxy dipole of a similar freeing of residually frozen cores. In these two cases $\chi(0)$ continues to increase with increasing temperature[7] which probably reflects the freeing of methoxy dipoles with the gradual 'melting' of end chain butyl groups. This does not happen in the case of the quenched nematic which indicates tangling of the butyl chains preventing any freeing of the methoxy groups after the cores have been reorganised.

We note that if the subsidiary loss process at 190 K to 220 K in cases A and C refer to the reorientation of the core dipole, then this is only possible over a limited temperature range during which the benzylideneaniline cores are mobile while adopting a new molecular configuration. Since the benzylideneaniline core in the stable state has only one orientation the effect of the waiting period at 200 K upon the subsequent metastable to stable transformation[4] rate possibly arises from the formation of stable state nucleii[2] while the cores are mobile, with the crystal growth itself only becoming rapid when the methoxy and butyl groups become sufficiently free.

SUMMARY

A brief description of the sequence of events occurring in MBBA during the three thermal histories investigated here gives the following descriptions;

(A) Slow cooling of the isotropic liquid crystal allows nematic ordering to set in, but the distribution of the director remains isotropic[16] and together with a random head to tail relationship of the methoxy and butyl groups will cause supercooling. A metastable solid is eventually formed with a structure in which steric interference between irregularly ordered methoxy and butyl groups forms regions of irregular order, best described in fractal terms as having an imperfect dilation symmetry. Heating causes a steady expansion of the lattice except for a slight disordering of structure around 150 K, and the number density of reorientable methoxy groups steadily increase. In the region of 200 K the small number of frozen benzylideneaniline cores become mobile and reorganise, freeing the core dipole tran-

siently and altering the density without changing the dilation symmetry. Further heating at a rate which is insufficient to allow stable state nucleii to grow regains essentially the same isotropic liquid crystal that the system originated from.

(B) Slow cooling of the nematic liquid crystal gives a metastable solid and no supercooling. This metastable state has a similar structure to that of case A, but with a smaller number density of regions of disorder due to the better anti-parallel packing of the methoxy groups, which is allowed by the improved head to tail ordering in the stabilised nematic liquid crystal. On heating a heterogeneous expansion occurs around 160 K, accompanied by a local structural reorganisation of the centres to a less ordered form. Further heating steadily increases the freedom of the methoxy groups without altering the symmetry of the defect centres. Again the small number of frozen benzylideneaniline cores become mobile, transiently, in the region of 200 K, freeing a greater density of methoxy dipoles. After melting the system returns to a nematic liquid crystal state which is stable to higher temperatures than is normal due to the elimination of core disorder in the cycle.

(C) Quenching the nematic crystal produces structural disorder approaching a perfect dilation symmetry. This structure is a nearly rigid matrix with the butyl end chains being constrained in motion as are the methoxy groups. A number of small re-arrangements disordering the structure and reducing the rigidity take place as the system expands on heating. The transient freeing of the benzylideneaniline cores in the region of 200 K allows considerable structural disordering of the centres to occur, but the restrictions upon the butyl chain conformations remain, preventing any extra freedom in the methoxy groups from being retained. On melting the system forms the isotropic liquid crystal rather than the nematic because the restraints of the end groups cause the benzylideneaniline cores to randomise in alternative orientations when mobile, rather than re-order, as in cases A and B.

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