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G. McMullin[a]; W. G. Scaife[a]; R. Zentel[b]
[a] Engineering School, Trinity College, Dublin 2, Ireland [b] Institut für Organische Chemie, Universität Mainz, Mainz, Germany

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Dielectric spectroscopy of an aligned liquid crystalline side chain polymer using high pressures

by G. McMULLIN, W. G. SCAIFE* and R. ZENTEL†

Engineering School, Trinity College, Dublin 2, Ireland

† Institut für Organische Chemie, Universität Mainz, D-55099 Mainz, Germany

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The complex permittivity of a liquid crystalline side group polymer has been measured at pressure from ambient up to 300 MPa. The samples were initially not aligned, then planar and finally homeotropically aligned by the field of a 7·2 Tesla magnet. Temperatures ranged up to 130°C, and measurement frequencies from 5 Hz to 5 MHz. The equilibrium permittivity ε_S has been interpreted in terms of an effective dipole moment μ. The frequency of maximum loss has been analysed in terms of enthalpy of activation and volume of activation for α and β relaxation processes.

1. Introduction

Liquid crystalline polymers with mesogenic side groups were first synthesized by Ringsdorf [1] and Shibaev [2]. Numerous studies have been carried out on two families of these materials, polysiloxanes [3, 4] and polyacrylates and polymethacrylates [5, 6], with a view to understanding their observed behaviour. For example, the length of the spacer connecting the mesogen to the polymer backbone has been varied, as has the terminal group of the side chain. Dielectric measurements have been made on materials that have been aligned either by using electric fields or magnetic fields at ambient pressure and at elevated pressures. The dielectric properties of a family based on polyacrylate and polymethacrylate main chains have been explored [5, 7–10]. One member of this group, figure 1, was prepared in a form suitable for experiments in cross-linking, with five per cent of the side groups substituted by an alkanol group [11]. The polymer deviates slightly from the phase behaviour of the corresponding homopolymer.

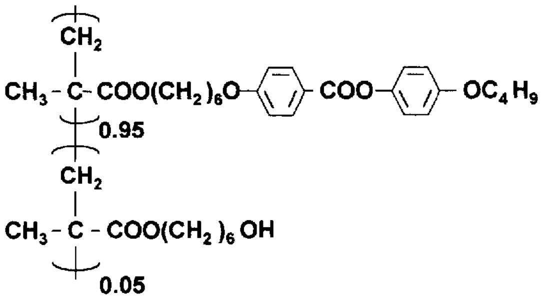

Figure 1. Chemical structure of liquid crystal polymer, sample 2 of [11].

This material has been examined in the non-aligned, homeotropically aligned and planar aligned states, at temperatures up to 120°C. Measurements have also been carried out at elevated pressures.

2. Experimental

The sample used had been prepared by Zentel [11] who had determined its phases by means of DSC and the use of polarizing optical microscopy. The glass transition occurs at 45°C, a smectic A phase exists at temperatures up to 102°C and a nematic phase exists up to a clearing temperature of 106°C. The molecular weight is estimated to be about 250 000.

Test capacitors were designed with the intention of subjecting the samples to intense magnetic fields, and to elevated pressures. A Hewlett Packard 4192A low frequency analyser was used to take scans of the parallel capacitance and conductance of the capacitor at frequencies between 5 Hz and 13 MHz. In order to connect the sample to the instrument the manufacturer has supplied a 1 m cable extension which has to be extended further to reach into the thermostat or pressure vessel as the case may be. This extension results in measurement errors which increase with the magnitude of the capacitance at frequencies above 2 to 5 MHz. The instrument does not measure capacitance directly, but admittance. This latter becomes very small at low frequencies and the instrument may then display capacitance values which are systematically too big [12]. To minimize this problem large values of capacitance are desirable. Clearly there are conflicting requirements on the size of the geometric capacitance, C_0,

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* Authors for correspondence.

of the capacitor. Values in the range 30 to 100 pF were used.

The first design, mark 1, was constructed using microscope slides on to which a 1 μm layer of aluminium had been evaporated to form electrodes. Metal was removed around the edges for a distance of 2 mm. Electrical connections were made using silver loaded epoxy cement. A weighed quantity of sample was melted on to the surface of the lower electrode, with a sprinkling of 50 μm glass spheres, in an evacuated chamber. The upper electrode was then lowered on to the sample, longitudinally displaced in order to facilitate access for connections. It was kept compressed until the assembly had cooled and the vacuum had been removed. A silicone gasket material was applied to the edges of the assembly in order to isolate the specimen from the oil used to pressurize the sample. A weakness of this design was a tendency for the electrical resistance of the epoxy connection to increase, giving rise to subtle errors. Also the encapsulating material tended to contaminate the specimen after a period of time.

A second design used metal cylinders with the end faces ground flat. A mark 2 version used 16 mm diameter tool steel cylinders and required spring loaded connections. A mark 3 variant of this, suitable for magnetic alignment, used 19 mm diameter cylinders of brass which allowed screwed connections to the electrodes. Filling of the capacitors was carried out as for the mark 1 design. To encapsulate the specimen, a tube of polyolefin 'heat shrink' material was shrunk on to the assembly. The choice of suitable diameters of tube and electrodes was based on experiment. The mark 3 design proved to be robust and trouble free.

The electrodes of the mark 2 cell were cleaned and treated with a solution of trichlorosilane in toluene, before spin coating with nylon 6/6. After drying, the two electrodes were rubbed with velvet and assembled in an antiparallel arrangement. The mark 3 assembly was placed in the 7·2 T magnetic field of an NMR instrument. The temperature was raised above the clearing point, and then allowed to cool slowly. The procedure was carried out on the same specimen with the field parallel to the electrode planes, and then with the field normal to them.

3. Complex dielectric permittivity

The complex dielectric permittivity $\varepsilon(\omega) = \varepsilon' - j\varepsilon''$ can be derived from measured values in terms of C_0 the geometric capacitance; $\varepsilon' = C_{\text{meas}}/C_0$, and $\varepsilon'' = G_{\text{meas}}/(\omega C_0)$. Only estimates of C_0 are available, especially at elevated temperatures and pressures, and so data are plotted as C_{meas} and G_{meas}/ω, and comparisons must be made in terms of $\tan\delta = C_{\text{meas}}/\omega G_{\text{meas}}$, which is independent of geometry.

The equilibrium, low frequency value of the permittivity, ε_S can be related to the dipole moment, μ of the material by means of the Kirkwood–Fröhlich equation [13],

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{4\pi N g \mu^2}{9kT}. \tag{1}$$

In this, ε_∞ is the relative permittivity at frequencies too high for the dipoles to respond, k is Boltzmann's constant and N is the number density of the dipole elements. The correlation factor g is greater than unity when dipolar orientation favours parallel alignment of neighbours, and is less for antiparallel alignment. It must be emphasized that in our case the value of μ is an effective average, being the summation of several different molecular sub-groups, and moreover our material is far from dielectrically isotropic.

The complex permittivity $\varepsilon(\omega)$ varies appreciably over the frequency band studied. Figure 2 shows a typical Cole–Cole plot. This can be represented as a combination of many relaxation processes, each with a characteristic relaxation time τ and corresponding strength. As the graph shows, the spectrum is very broad, and can be represented by the empirical correlation of the Havriliak and Negami equation [14],

$$\varepsilon(\omega) - \varepsilon_U = \frac{(\varepsilon_R - \varepsilon_U)}{(1 + (j\omega\tau)^{1-\alpha})^{\beta}}. \tag{2}$$

In this ε_R represents the permittivity at frequencies very far below the peak of ε'' and ε_U represents the permittivity at frequencies very far above this peak. Where different relaxation processes are widely separated in frequency, this equation can be fitted to each. Only when the fit extends from the lowest to the highest frequencies to which dipoles can respond does $\varepsilon_R = \varepsilon_S$, the equilibrium

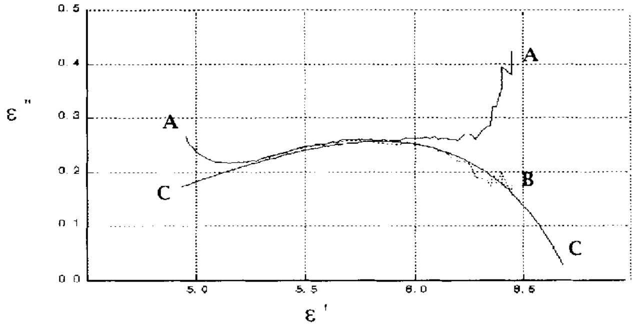

Figure 2. Cole–Cole plot of a planar aligned sample at 75°C showing (*A*) raw data, (*B*) data with d.c. conductivity subtracted, and (*C*) equation (2) fit. Note: no corrections have been made for high frequency artefacts.

permittivity, and $\varepsilon_U = \varepsilon_\infty$. In fitting this equation to measured ε'' data, an interactive computer program was used [15]. This included a provision for subtracting the contribution at low frequencies due to ionic conductivity,

$$\varepsilon''(\omega) = \frac{\sigma_0}{\varepsilon_0 \omega^{(1-s)}}. \tag{3}$$

In this ε_0 refers to the permittivity of free space, while σ_0 and s are fit parameters. Since this expression implies a frequency dependence, it is a matter of judgement when conductivity must be distinguished from a low frequency relaxation process. The superiority of the mark 2 and mark 3 cell designs over the mark 1 was of importance, because it avoided contamination of the sample by encapsulating material, with a consequent increased ionic conductivity. The correction required by equation (3) was therefore much reduced.

It may be remarked that equation (2) is merely a data correlating expression, and the parameters used to fit ε'' data, namely α, β, τ, and $(\varepsilon_R - \varepsilon_U)$ have more uncertainty individually than for example the value of frequency $f_{\max}$ at which ε'' reaches a maximum, or the half width of the loss curve which is predicted by equation (2) which involves all the fit parameters. The relative smallness of the values of ε'' in figure 2 prevents accurate measurements at the highest frequencies.

4. Equilibrium permittivity

The effect of temperature on $\varepsilon'(\omega)$ of a sample that has not been subjected to alignment treatment can be seen in the isochrones of figure 3. What is notable is the rise of ε' with temperature, whereas equation (1) would suggest a decline in the equilibrium permittivity ε_S. It has been established [5, 7] that a number of relaxation processes occur in this material in the frequency range used for these observations, and so it is expected that $\varepsilon'\varepsilon'' \neq \varepsilon_S$. At those temperatures where equation (2) could be fitted, a reasonably good estimate of $C_0\varepsilon_S$ was made as follows. The measured value of C was taken at 20 kHz, and to this was added a quantity calculated from equation (2), namely $(\varepsilon_S - \varepsilon')C_0$ where ε' was calculated for 20 kHz also. The choice of 20 kHz was made to avoid frequencies where the precision of measurement was doubtful. Figure 4 shows the values of C corresponding to $C_0\varepsilon_S$ as a function of temperature for a sample in the brass cell in different states of alignment. At temperatures just above the glass transition, it was not possible to determine the contribution of the low frequency α relaxation and therefore ε_S.

Using a similar approach, it is possible to estimate a value of ε_U for the β relaxation in the glass phase. In the range of temperatures between 25° and 40°C estimates derived from both aligned and unaligned samples in the mark 3 cell concur to within ± 2·5 per cent on a value of 3·48. This is greatly in excess of n^2, which implies the existence of a further, higher frequency relaxation termed γ in [5].

Confirmation of the estimates of C_0 for the mark 3 cell, based on dimensional measurements, was obtained by comparing values of ε' for the corresponding homopolymer, given by Braun [16], at several frequencies and temperatures, with values of C_{meas} taken from a sample in the non-aligned state. The values of C_0 are estimated to have an accuracy of ± 10 per cent, sufficient to permit the exploration of the behaviour of ε. Measured values of specific volume $v(pT)$ are not available for this material, but a very similar polymer, 2 of [17], has been studied over a range of temperatures and pressures. The difference between the two polymers lies only in the end group of the mesogenic side chain which is OCH_3 in the other case. This difference changes the glass temperature slightly and causes the smectic A phase to be replaced by a nematic phase, but with a similar temperature span. Using these

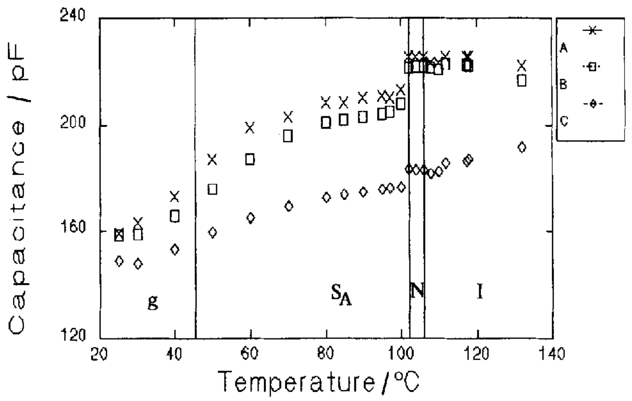

Figure 3. Capacitance of a non-aligned sample at different frequencies as a function of temperature, (*A*) 100 Hz, (*B*) 1 kHz, (*C*) 1 MHz.

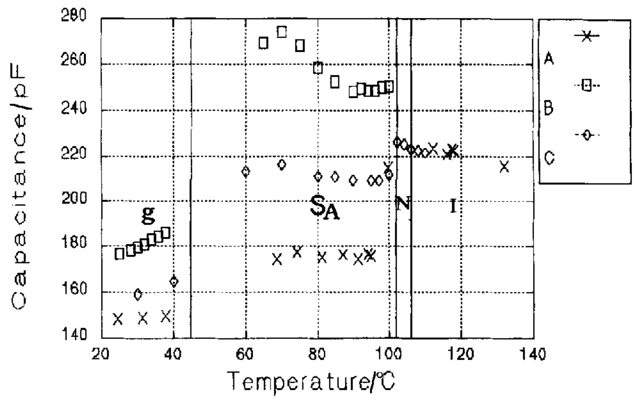

Figure 4. $\varepsilon_S C_0$ as a function of temperature for different sample alignment states, (*A*) homeotropic, (*B*) planar, (*C*) not aligned.

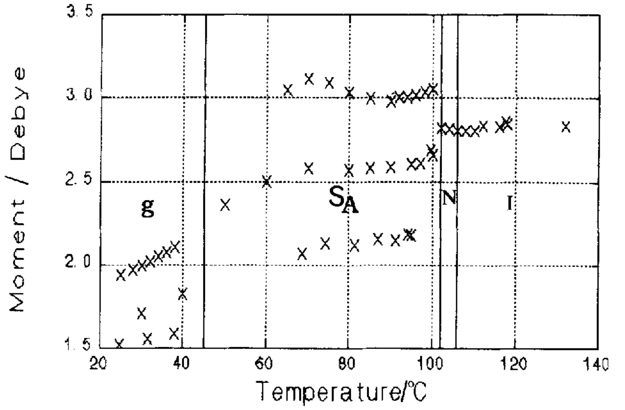

Figure 5. Dipole moment μ, calculated assuming $\varepsilon_\infty = 2{\cdot}75$, calculated for sample in different states of alignment. Top data, planar; bottom data, homeotropic; intermediate values, non-aligned.

data, it is also possible to estimate the effect of temperature and pressure on C_0 by assuming that the area occupied by the specimen remains essentially constant, and that changes in pressure and temperature affect the spacing only. This of course ignores any anisotropy in the mechanical behaviour of the aligned material.

With values of ε_S so derived, equation (1) can be used to show how the effective dipole moment μ behaves. There is some uncertainty about the appropriate value of ε_∞ to be used when estimating μ, something close to the square of the refractive index would set a lower limit. But although the absolute magnitude of μ is strongly dependent on the choice of ε_∞, as well of course as on $v(p, t)$, the trends with changing temperature and type of alignment are unaffected. Changes in ε_∞ with pressure and temperature have been calculated on the assumption that it obeys the Clausius–Mossotti equation. Figure 5 has been plotted for an intermediate value of $\varepsilon_\infty = 2{\cdot}75$, and it can be seen that there is a close resemblance to figure 4.

5. Relaxation behaviour

Previous work on the corresponding homopolymer [5, 7] has shown that the dielectric response is characterized by a high frequency, β process which is discernible with our equipment at relatively low temperatures. A second, low frequency, α, process becomes evident above the glass transition temperature. It has also been suggested [5] that an even lower frequency, δ, process of small amplitude can be discerned at temperatures in the neighbourhood of the nematic phase.

As figure 2 makes clear, the α relaxation process is very broad. The half width of the ε'' plot is generally between three and six decades wide, and often extends beyond the range accessible to our instrumentation. The actual width of the ε'' spectrum changes significantly with temperature and pressure, which suggests that it is a composite of two somewhat narrower curves which each have different temperature and pressure sensitivities. In this respect it behaves like poly-*n*-butyl methacrylate [18], a non-liquid crystalline polymer.

In order to discuss the effect of temperature and pressure on the frequency $f_{\max}$ at which ε'' reaches a maximum, the theory of absolute reaction rates will be used. Here $\tau \equiv 1/2\pi f_{\max}$, and the so-called activated state is symbolized with ‡. The effect of temperature is represented by the activation enthalpy $\Delta H\ddagger$,

$$\Delta H\ddagger = R(\partial \ln T\tau)/\partial T^{-1})p \tag{4}$$

and the pressure by the activation volume $\Delta V\ddagger$,

$$\Delta V\ddagger = RT(\partial \ln \tau/\partial p)_T. \tag{5}$$

6. Alignment

The effect of a magnetic field is to tend to orient benzene rings with their planes parallel to the field lines. A computer model of the side chain [19] suggests that while the planes of the two rings lie at the angle of 30° or so to one another, their *para*-axes lie roughly in line, and parallel to the long axis of the mesogen. A minimum energy orientation therefore requires that the long axis should lie along the magnetic field direction. The specimen which was subjected to a magnetic field in a direction which is normal to the electrode planes therefore takes up a homeotropic orientation. The specimen subjected to a field parallel to the electrode planes will have planar orientation. The effect of this can be seen in the behaviour of $C_0\varepsilon_S$, as, for example, in figure 4. The sequence of events with the mark 3 cells was as follows; ambient pressure measurements in non-aligned, homeotropically aligned and then planar aligned states. These were followed by pressure measurements which never extended to the iostropic condition.

A calculation of the expected, non-aligned value of $C_0\varepsilon_S$ can be made, giving $1/3(2C_{\text{planar}} + C_{\text{homeo}})$. This proves to be 6–7 per cent higher than the measured value, whether at 30°C or at 90°C. In order to account for this, C_0 values would have to differ by 10 per cent, and this seems improbable. One possibility is that the homeotropic alignment could have been less than complete. Alternatively the non-aligned sample had some extra degree of homeotropic alignment. This seems probable since the calculated value just below the nematic transition agrees very well with the measured value in the isotropic state at 108°C.

A comparison was made between the capacitance readings taken at 1 MHz with the mark 2, nylon coated cell, and those of the mark 3 cell over a range of temperatures from 25°C to 90°C. This showed that in comparison to the case of the planar orientation, there was virtually no systematic variation in the ratio of capacitance of the two cells with temperature. This contrasted with a strong temperature effect when comparison was made with the homeotropic specimen. It is concluded that the nylon coating favoured a planar alignment. This is like the behaviour after PVA coating [20].

7. Results

X-ray measurements have been carried out on fibres of the corresponding homopolymer in which the polymer main chain had been oriented by drawing from a melt [6]. These have established that in the smectic A phase the lattice spacing is 28 Å, slightly longer than the length of the mesogenic side group, 27 Å, which implies a monolayer structure. If the backbone is in an all *trans*-configuration, the mesogenic groups will lie on top of each other in an antiparallel arrangement, and a close packed hexagonal structure is possible for them. This agrees with the observed lattice spacing of 4·4 to 4·5 Å. Since our dielectric measurements agree well with those for the homopolymer, we assume that our material has a similar structure.

There are several dipolar groups to be considered, see figure 1, including the 5 per cent or so of hydroxyl side chains. In the smectic A phase, and in the glass state reached by cooling from this ordered state, the mesogenic core will be constrained, being able to rotate only about its long axis, and will be restricted in rotation about its short axis. The dipole moment associated with the phenyl benzoate group will be most evident in dielectric measurements when the long axis is perpendicular to the electric field, i.e. in the planar orientation. This group is surrounded by benzene rings as nearest neighbours.

Rotation of the dipole moment of the terminal, butoxy, OC_4H_9 element of the side chains will be about the *para*-axis of the benzene ring, and therefore less evident in the homeotropic orientation. Finally the motion of the dipole moment associated with the methacrylate group will be determined to a large extent by the freedom of movement allowed to the main chain. It will therefore be more evident in dielectric measurements above the glass temperature. The orientation of the main chain will be influenced by that of the side chains and so the effect of the main chain dipole moments may also be sensitive to the orientation imposed on the side chains.

The behaviour of ε_S as a function of temperature can be inferred from figure 4. It shows that, whereas below the glass transition there is little change in the case of the homeotropic sample, for the planar sample ε_S rises steadily with temperature. The 20 to 25 per cent increment in ε_S in the glass phase must be attributed to vestigial freedom possessed by the side chain dipole even in the glass phase. It becomes evident in the planar orientation and is associated with the β process. At the glass transition, there is an increase in ε_S for both orientations, but this is most pronounced in the planar orientation. Because of experimental limitations it was not possible to estimate values for the oriented samples between 40° and 60°C. Beyond this point, a small decline with temperature can be discerned in the planar case, but not in the homeotropic sample. At the nematic transition, values of ε_S for all the samples converge and follow a similar slowly declining trend as the temperature is raised. No change is visible as the clearing temperature is exceeded.

Bearing in mind the uncertainties discussed above, some conclusions can be drawn about the effective dipole moment μ, see figure 5. In the glass phase of the planar sample, it tends to increase with temperature. This may be attributed to an increase in the numbers of side chains which acquire sufficient freedom to rotate about their long axes. There is a significant rise on entering the smectic A phase in the case of both orientations, but this is much greater in the planar sample. Within probable error, it can be said that μ does not change in this phase as the temperature increases. At the transition to the nematic phase, μ falls to a value between that observed in the planar and that in the homeotropic oriented smectic A state. It remains essentially constant from this point until well into the isotropic state at 132°C.

The planar orientated sample was subjected to pressure runs at three temperatures. At 90° and 98°C, the pressure was raised from 0·1 MPa to 300 MPa. The temperature was then increased to 110°C keeping the pressure at 300 MPa, after which it was lowered to 50 MPa. The sample was then cooled returned to ambient temperature and its pressure reduced to ambient.

Where it was possible to fit equation (2), estimates of $\varepsilon_S C_0$ have been made and the corresponding values of μ are shown in figure 6. In general there is a tendency to increase for all samples up to 150 MPa. Above this pressure, only

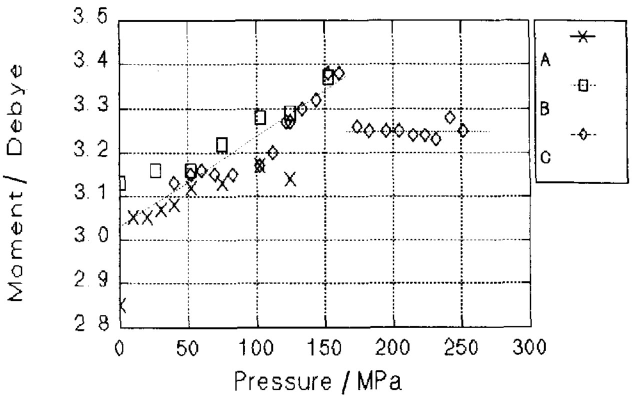

Figure 6. Effective dipole moment μ as a function of pressure for planar aligned condition, (*A*) at 90°C, (*B*) at 98°C and (*C*) at 110°C. Dotted lines are guides only, $\varepsilon_\infty = 2{\cdot}75$.

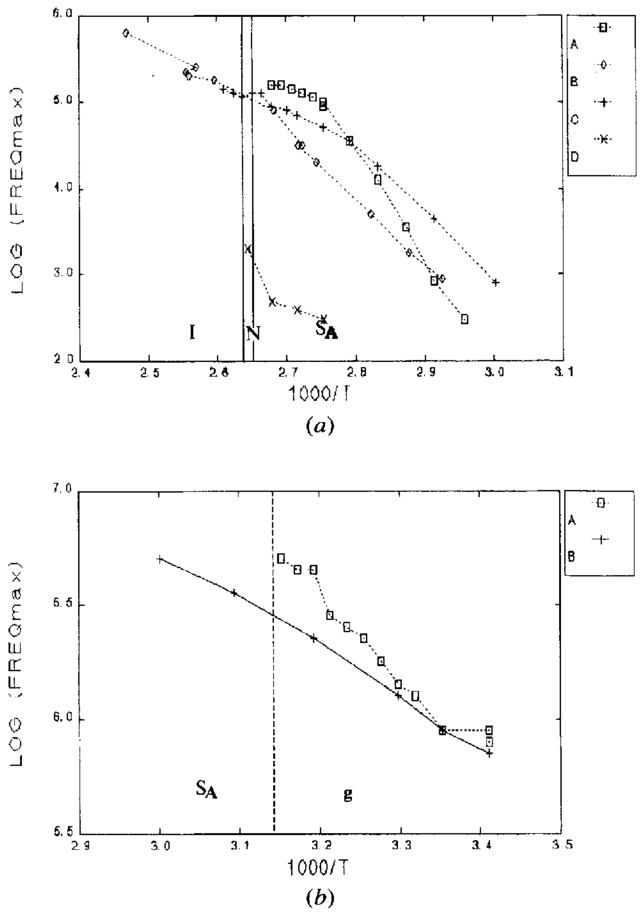

Figure 7. (*a*) Effect of temperature on $f_{\max}$, for α relaxation, curves (*A*), (*B*), (*C*), and δ relaxation curve (*D*). Alignments, (*A*) and (*D*) planar, (*B*) homeotropic and (*C*) non-aligned. (*b*) Effect of temperature on $f_{\max}$, for β relaxation. Curve (*A*) planar aligned and (*B*) non-aligned sample.

data at 110°C are available, and show a constant value, somewhat lower than the peak. This change at 150 MPa suggests a raising of the glass transition temperature as pressure is applied. But the corresponding slope of 2·3 MPa deg^{-1} for the glass transition temperature, compares with 5 MPa deg^{-1} measured for polymer 2 of [17].

At relatively low temperatures, it is the β relaxation which can be observed at our experimental frequencies. For the sample in a non-aligned condition, the half width of 2·3 to 2·9 decades compares with the figure of 2·56 quoted for the corresponding homopolymer [7]. The data for the non-aligned sample in the mark 1 cell coincided so closely with those for the mark 3 cell that they were omitted for clarity in figure 7 (*b*). The temperature sensitivity of $f_{\max}$, corresponds to $\Delta H\ddagger = 38\,\mathrm{kJ\,mol^{-1}}$ compared to 54 kJ mol^{-1} for the homopolymer. The planar aligned sample yields a higher value of 71 kJ mol^{-1}, and half-widths of 3·0 to 3·1 decades. The amplitude of this relaxation in the homeotropic alignment was well below one half that in the planar and the non-aligned states at 25°C, and values for neither $f_{\max}$ nor $\Delta H\ddagger$ could be established.

The effect of temperature on the α process relaxation frequencies $f_{\max}$ can be seen in figure 7 (*a*). The homeotropic sample has an Arrhenius behaviour with $\Delta H\ddagger = 148\,\mathrm{kJ\,mol^{-1}}$. From 70° to 100°C, the half width of the ε'' curve falls from 4·6 to 3·6 decades. The curve in the nematic and isotropic states continues smoothly from this point, with a slope corresponding to $\Delta H\ddagger = 75\,\mathrm{kJ\,mol^{-1}}$. The half width is 4 in the nematic, and 3·3 in the isotropic phase.

The planar sample behaves in a similar manner, but with $\Delta H\ddagger = 236\,\mathrm{kJ\,mol^{-1}}$ at temperatures up to about 85°–90°C. The graph then curves over to become virtually horizontal. The half width values rise from 4·8 at 65°C, to 6·4 to 75°C, then fall to 3·8 at 100°C. As can be inferred from figure 5, the value of $\varepsilon_R-\varepsilon_U$ is much larger for the planar sample than for the homeotropic sample.

The non-aligned sample shows higher values of $f_{\max}$ than the homeotropic sample, but an almost identical slope at lower temperatures. However, above 85°C, curvature increases, so that $\Delta H\ddagger$ is 67 kJ mol^{-1} until the graph merges with the others in the nematic state. The half width falls from 5·1 at 50°C to 4 at 100°C. In the nematic phase it is close to 3·4 and in the isotropic it is 3·1 decades.

The small value of C_0 and the presence of appreciable ionic conductivity, made it difficult to discern the δ process which has a lower $f_{\max}$ than the α relaxation; nevertheless at some temperatures above 90°C, an estimate could be made. It was found that for a planar aligned sample in the mark 2 cell, the values of $f_{\max}$ are up to two orders of magnitude smaller than for the α process. The amplitude $\varepsilon_R-\varepsilon_U$ was about one quarter that of the α relaxation and the half width of the ε'' curve was well below two decades. This narrow half width has also been observed in other materials exhibiting a δ process [9, 10, 21].

It was noticed that when a fit to ε'' data was made including a δ process as well as an α relaxation, the value of $f_{\max}$ obtained for the α relaxation was significantly bigger than when the δ process was ignored. The curve of $f_{\max}$ for the α process in the planar aligned sample in figure 7 (*a*) was plotted from data fits which ignored the δ process. Consequently the change in slope as the temperature rises towards the S_A to nematic transition may in part at least be due to disregard of this fact.

8. Pressure effects

In the case of the α relaxation, the effect of pressure on $f_{\max}$ for a planar aligned specimen is shown in figure 8. It corresponds to values of $\Delta V\ddagger$ ranging from 100 cm^3 mol^{-1} at 90°C to 92 cm^3 mol^{-1} at 98°C and 91 cm^3 mol^{-1} at

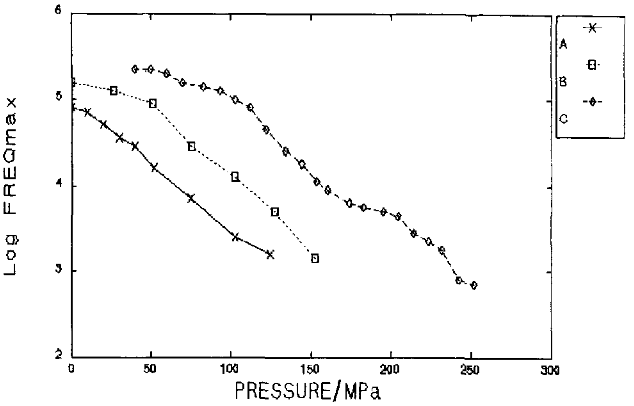

Figure 8. Effect of pressure on f_{max} for planar alignment. Curves (*A*), (*B*) and (*C*) correspond to temperatures of 90°C, 98°C and 110°C, respectively.

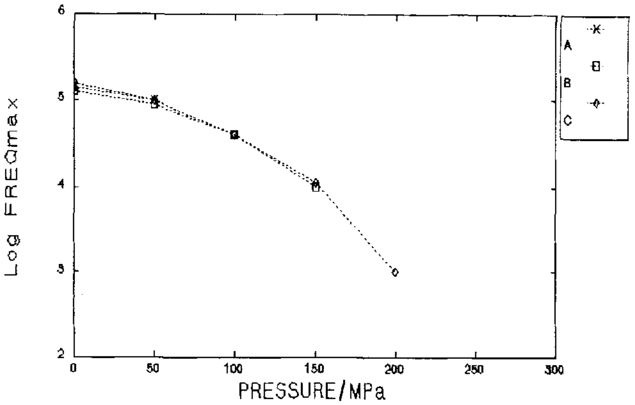

Figure 9. Effect of pressure on f_{max} for non-aligned sample. Curves (*A*), (*B*) and (*C*) correspond to temperatures of 100°C, 105°C and 110°C, respectively.

110°C. This is equivalent to 25 per cent of the molar volume of the repeating unit. Heinrich and Stoll [8] examined a polyacrylate, P/H/6/CN, with a side chain which differed from our side chain only in that it terminated with a CN group. For the α process, at 80°C and 120°C, the value of $\Delta V^{\ddagger}$ ranged from 49 to 31 per cent of the repeating molar volume. They found that the lower frequency, δ process behaved in a very similar manner. Observations on a polysiloxane in which the side chain was terminated with a CN group, and which had been aligned homeotropically by an electric field [3], also relate to a δ process. Between 50° and 70°C, $\Delta V^{\ddagger}$ approximates to 32 to 29 per cent of the repeat unit volume, and $\Delta H^{\ddagger}$ to 125 kJ mol^{-1}.

At 90°C the half-width remained close to 5·2 decades at pressures from 0·1 MPa to 125 MPa. At 98°C it increased from 4·2 at 0·1 MPa to 5·8 at 152·5 MPa, and at 110°C, from 40 to 100 MPa, the half width was 4·4 decades. It then rose 5·9 at 160·5 MPa. Between 195 and 252 MPa it remained close to 5·1 decades.

Measurements were made on a non-aligned sample in the mark 1 cell at pressures up to 300 MPa and temperatures from 100° to 110°C. These give values of f_{max} which are close to those of the mark 3 cell. Application of pressure decreases f_{max}, but the slope $(\delta \ln f_{max}/\partial p)_T$ increases with pressure, see figure 9, which is in line with the measurements of [8] on a non-aligned sample. The general effect of pressure is to increase the half-width of the relaxation curve.

Estimates of f_{max} for the β relaxation were also obtained for this non-aligned sample. These correspond to $\Delta V^{\ddagger}$ of 16·3 and 17·8 cm^3 mol^{-1} at 25°C and 40°C. In the smectic A phase, values of 16·5, 17, and 19·5 cm^3 mol^{-1} were found for 50°, 60° and 70°C. Analysis of the data suggests that $\Delta H^{\ddagger}$ declines from 45 kJ mol^{-1} at 25°C to 33 kJ mol^{-1} at 200 MPa, and then rises to 39 kJ mol^{-1} at 300 MPa. In the glass phase, the half-width of the ε'' curve rises with pressure from under 3 to 4 at 300 MPa. Raising the temperature reduces half-width, so that above 70°C it is less than 3 at all pressures.

The magnitude of the residual, zero frequency, ionic conductivity in our mark 3 cell only exceeded the minimum discernible value by a significant amount at temperatures above about 75°C. It then exhibited an Arrhenius temperature dependence with an energy of 110 kJ mol^{-1}. This is somewhat less than that estimated for a polysiloxane side chain polymer [21], and extrapolating to lower temperatures, we find our material to be less conducting.

Typically 2 hours or more elapsed between readings, and time was assumed not to be a variable in the analysis of data. There is however some evidence of a change being caused by application of pressure which persisted after its removal. The mark 1 cell was raised to a pressure of 300 MPa at 80°C. On returning to 100 MPa, there was no discernible change in $\tan\delta$ or C_{meas}. But at 50 MPa and at 0·1 MPa a clear reduction in $\tan\delta$ had taken place above 100 kHz, with a corresponding rise below 10 kHz in figure 10. This was due almost entirely to changes in ε'', rather than ε'. A second example of a long lasting effect was observed in measurements made on the planar aligned sample. Comparing initial measurements with data taken after temperature and pressure excursions, it is clear that a new low frequency peak in ε'' had appeared, see figure 11, even though the sample remained in a planar alignment.

9. Discussion

The calculation of a value for the effective dipole moment of one unit of the polymer and its side chain is difficult. But if it is assumed that in the isotropic phase, all the dipolar groups are free to rotate independently, and the data quoted by Klingbiel *et al.* [22], are used, then a value of μ of 3·3 to 3·4 D is obtained. This compares well with

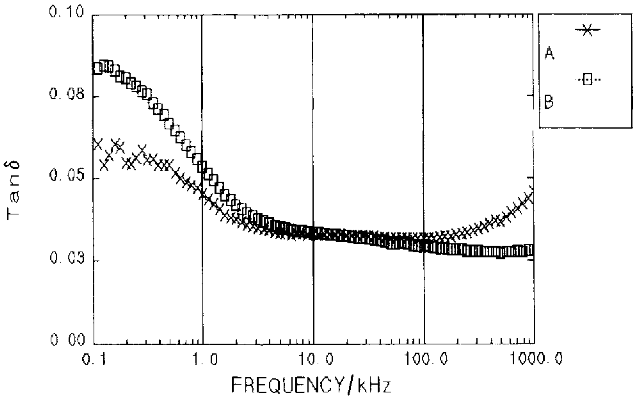

Figure 10. Non-aligned sample, mark 1 cell at 0·1 MPa and 80°C, (*A*) before and (*B*) after excursion to 300 MPa showing the hysteresis in tan *δ*.

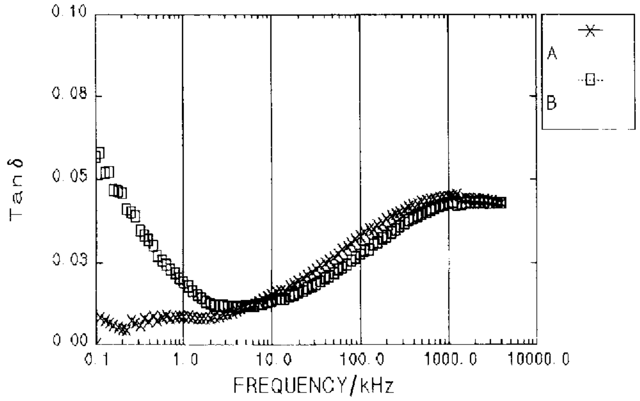

Figure 11. Planar aligned sample in mark 3 cell at 25°C. Low frequency relaxation: (*A*) before and (*B*) after temperature excursion up to 110°C. Above 98°C, pressure was always above 50 MPa.

figure 5. If the value used for ε_∞ is changed from 2·75 to 2·2, then the measured estimate rises to 3·4 D. The enhanced value of μ in the smectic phase of the planar aligned sample is consistent with a situation in which some of the constituent dipoles, those connected to the two benzene rings and with vector components perpendicular to the long axis of the mesogen, are constrained to move so that they trace out a disc in space. By contrast, in the isotropic state, these dipoles trace out the space within a sphere.

The response of the β relaxation to the application of pressure and to alignment, is consistent with its assignment to the phenyl benzoate dipolar group [5], [9]. The relatively large value of $\varepsilon_U = 3{\cdot}48$ which we obtain for this relaxation makes it plain that other, higher frequency relaxations must exist, beyond our range of measurement. These may be related to rotation of the butoxy group. The difficulty of estimating the relaxation parameters in the homeotropic state may be in part due to the bigger $f_{\max}$. It may in fact be a γ process.

The effect of magnetically aligning a polyacrylate which has a side chain identical with our material, except that the terminal group, OCH_3, is shorter, has been reported by Bormuth *et al.* [9]. This shows that the planar aligned sample has a very broad α process. The homeotropic alignment by contrast reveals a much narrower δ relaxation at lower frequencies, with a somewhat smaller peak value of tan δ. It shows a clear increase of ε_S on going from the smectic phase at 76°C to the isotropic phase at 118°C. On the basis of low frequency values of ε', it is reported that ε_S should increase with temperature in the smectic phase. A glance at our figures 3 and 4, shows that this need not be so.

In the planar alignment, their values of tan δ are somewhat bigger than ours. Plots of $f_{\max}$ show Arrhenius behaviour with a slope of 57 kJ mol^{-1} for the β process. In the smectic phase the value for the α process in the planar orientation is given as 330 kJ mol^{-1}. The activation energy for the δ process in the homeotropic orientation is smaller at 140 kJ mol^{-1} in the smectic and nematic phases. Similar measurements on a polychloracrylate with the same side chain as our material showed that a broad α process was evident in both orientations. It would appear that the chlorine atom has a similar effect to the methyl group on the behaviour of the polymer backbone, and in the homeotropic alignment converts the narrow δ relaxation to a broad α relaxation.

Two other side-chain polyacrylates have been magnetically orientated by Haase *et al.* [10]. These have a CN group in place of the terminal OC_4H_9 and correspondingly bigger values of ε. One of the pair has a side chain which is otherwise identical to ours. It has a nematic mesophase. In a homeotropic alignment, the low-frequency process is a narrow δ relaxation. In the planar state, a much broader α process appears with a value of $f_{\max}$ which is two decades larger. Although the relaxation in the homeotropic alignment is a narrow δ, unlike our broad α process, the activation plots for α and δ processes show some similarities. The relaxation in the homeotropic alignment for both have an Arrhenius character with almost equal values of $\Delta H\ddagger$, despite the difference in half-widths of the relaxation processes. Similarly the planar aligned samples both show a tendency for the plot to level out at higher temperatures. The value of $\Delta H\ddagger$ in both is much higher than for heterogeneous alignment, but is not quantified for Haase's material.

Experimental limitations imposed by the presence of ionic conductivity at higher temperatures make it difficult to identify a δ process in our data. In figure 7 (*a*) it is shown for a planar aligned sample, but is very weak. What is surprising is that in terms of $\Delta H\ddagger$, there is little difference between our material and other aligned polyacrylates, despite the much lower frequency and narrower relaxation curve which distinguishes the δ from the α process. This strongly suggests that the molecular motions revealed by dielectric measurements are very similar for both. The apparent absence of a broad α relaxation in Haase's homeotropic material may simply be due to the obscuring effect of its much stronger δ process. As is pointed out in [10], the broad α relaxation will be the composite of movements of several dipolar groups. The two ester groups would be expected each to have a half-width typically of three decades [18].

The effect of pressure as judged by $\Delta V\ddagger$ is similar for the α process in our planar orientation to that in both the α and δ processes of the non-aligned polyacrylate of [8] and the homeotropically aligned polysiloxane of [3]. Even the response of a homeotropically aligned sample of low molar mass liquid crystal 5CB is broadly similar, with $\Delta V\ddagger$ at 25 per cent of molar volume [23]. In the latter case, the narrow half-width of the relaxation reflects the uniformity imposed by the nematic potential as it forces rotations to be always close to 180°C. It seems not unreasonable to suppose that there are similarities in the molecular behaviour of each of these materials. If it involves rotation of the side chain about the backbone, this will tend to a single relaxation frequency provided the motion has a degree of regularity. Where such uniformity is absent, as in a planar aligned material like 5CB when it rotates about its long axis, then a broad spectrum is expected. The presence of a methyl group or a chlorine atom at the point where the polymer backbone is joined to the side chain seems to cause a lack of regularity in such side chain movements. Alternatives to the explanation of the δ process have been advanced—collaborative motion of the dipole vectors tracing out the surface of a cone, for example [3]. A similar suggestion has been made on the basis of infrared measurements [24]. Such behaviour should yield $g > 1$ in equation (1), with a visible enhancement in ε_S.

The detection of a weak, narrow, δ relaxation in a planar sample, figure 7 (*a*), must relate to something different. Perhaps it is associated with fractions of material at the end of chains, or at boundaries of domains where constrictions of structure are less effective. In this connection, consider the apparent change produced in a sample by an excursion to high pressures, see figures 10 and 11, where a low frequency relaxation appears at the expense of a much higher frequency process. Another way of stating this is that events relaxing a disturbance have become less likely than before, and the relaxation time is longer. This would be compatible with the reduction of the extent of disordered regions.

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