Dielectric relaxation spectroscopy studies on a polymer with mesogenic side chains

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The dielectric relaxations and the optical transmission of a carefully purified liquid crystalline side chain polysiloxane have been measured in the isotropic and the nematic phases, and an apparent hysteresis has been found in the biphasic region during cooling and warming cycles. In the biphasic region the rate of mesophase formation during cooling was found to be accelerated by an aligning field. Planar alignment was achieved, and the pure α process observed. The sample formed a gel upon lengthy heating, but it remained a liquid crystal. In the mesophase of the gel the α relaxation process was restricted in amplitude and the δ process was absent.

(Keywords: liquid crystalline polymer; high purity; mesogenic side chain; optical transmission; dielectric relaxations; alignment; gel formation)

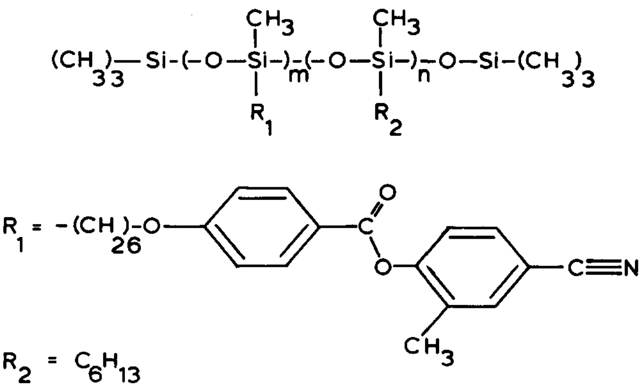
INTRODUCTION

In comparison with low molecular weight mesogens, liquid crystalline polymers, which have mesogenic groups as side chains, have much longer response times to electrical and to mechanical stress, on account of their higher internal viscosity[1–4]. The effect arises from the presence of the main chains of the polymer backbones, and is also present in solutions of mesogenic polymers in low molecular weight liquid crystals[5,6]. Such polymeric liquid crystals may not be used in display devices, where a rapid response to an electric field is required, but may be used as information storage materials[7–9], since their dielectric and optical properties stay constant for long periods of time after they have been aligned in an electrical field. This is so not only when the polymer is in the glassy state, but also when it is somewhat below the clearing temperature of the mesophase.

To permit *inter alia* the proper investigation of these phenomena with the polysiloxane class of liquid crystalline side chain polymers, attention has been directed to enhancing the yield of the grafting reaction and to removing the excess of monomeric mesogen after the preparation. An extremely pure form of one polymer has been produced by precipitating the polymer eight to ten times into a non-solvent to remove the impurities of side chain precursor[10]. The first experiments on the dielectric properties have shown that the impurity had the effect of plasticizing the motions of the mesogenic groups attached to the polymer chain[11]. To overcome the absence of the plasticizing effect upon the motions of the side chain mesogenic groups in the highly purified polymer, as measured by the frequency of the loss maxima, a temperature rise of ~9°C was required[11]. It was still possible to align the purified polymer.

Here we explore more fully the dielectric relaxations of a second carefully purified polysiloxane. We describe how it may be planar aligned and we report measurements made simultaneously with the dielectric study of the optical transmission of a film of the sample. During its manipulation at elevated temperatures the sample formed a gel on two occasions, with novel and interesting consequences for the dynamics of the side chain units. Transforming the material from a pure linear polymer into a crosslinked network has modified the response of the polar units to a probing electric field.

The polymer used in the study, LCP6 (*Scheme 1*), was provided by G. W. Gray and his colleagues at Hull University. It had mesogenic units, formed from a twin aromatic ester structure that carried a polar nitrile group, which were linked by an oligomethylene spacer to a short polysiloxane chain ($m+n \approx 35$, $m \gg n$). The mesogenic units had been grafted onto the siloxane chain with the aid of a chloroplatinic acid catalyst, and after this treatment the small proportion of remaining Si–H sites on the backbone had been similarly reacted with an excess of n-oct-1-ene in an attempt to remove them.



Scheme I

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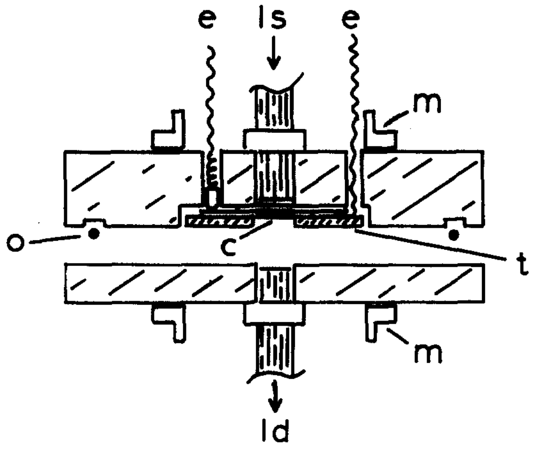

Figure 1 The cell equipped for simultaneous studies of light transmission and dielectric loss. The glass cell, c, is held in a Tufnol mount, t, between two brass pieces held together by a threaded screw and sealed by the 'o' ring, O. Two mounts, m, carry the copper tubes that protect from the water of the thermostatted bath, the electrical leads, e, and the light guides, ls and ld, from the light source and light detector. The cell was set with the polymer film mounted vertically

Subsequently, the unattached mesogen impurities had been carefully removed from the polymer by reprecipitation at least eight times from solution by pouring the polymer into the non-solvent methanol[10]. When applied to another polymer the procedure had reduced the proportion of unattached mesogen to <0.06%, the detection limit of the thin layer chromatography technique that was used for analysis[12]. The polymer had a clearing temperature of 53°C when examined optically and when examined by differential scanning calorimetry (d.s.c.) cleared over a range 51–59°C, which is about 8°C higher than a similar sample that had not been so carefully purified[13,14].

EXPERIMENTAL

Before the polymer was placed in a cell, it was degassed in vacuum at 110°C for 3–4 h. After the sample was placed within a cell, it was held at 75°C for at least 2 h in the thermostatically controlled water bath before the measurements were made.

Measurements of dielectric loss between 12 and 10^5 Hz and studies on the alignment of the mesogenic phase were made on the sample as a disk of diameter 1.1 cm in a three terminal brass cell with a 100 μm space between the freshly polished electrodes, as has been described before[11,13–17], using a General Radio precision RLC 1689 Digibridge controlled by a microcomputer. The standard dielectric response obtained was G/ω, which is proportional to the dielectric loss plus any conductivity of the sample, and was plotted automatically by the microcomputer. Conductivity decreased approximately inversely with measurement frequency, and was a negligible factor with this polymer sample.

The polymer was also studied in a glass cell formed from slides that had 1 cm square transparent conducting surfaces, between which there was a 25 μm cavity created by a Mylar spacer, to permit simultaneous studies of optical transmission and of dielectric loss. The cell (*Figure 1*) was mounted in a Tufnol fitting inside a brass holder that could be placed in a thermostatted water tank. Within a copper tube, screened leads linked the cell to the bridge for electrical measurements and two non-coherent glass fibre light guides, each 50 cm long and of 60 mm diameter, were used to transmit light to and from the cell. A third light guide provided an external reference beam. A light sensitive diode was placed at the end of each beam and the difference between the outputs of these two sensors was led to a paper chart recorder. Voltage differences of about 0.5 V, which might be displayed as a deflection of 10 cm, were obtained on passing through the nematic to isotropic transition. In the recorder's most sensitive mode, reversible changes of the order of 1 mV were recorded as deflections of 20 (±1) mm on the paper. Below the biphasic region of the LCP6 sample, a small temperature rise in the bath led to a response in optical transmission about 60 s later. The signal took ≈10 min to settle to the new equilibrium value, which was the maximum time required for the bath and cell assembly to reach a new temperature. Then the dielectric measurement was made.

RESULTS AND DISCUSSION

Dielectric measurements

When the dielectric response of the sample in the brass cell was examined in the isotropic phase, the single loss peak was not quite symmetrical, having a tail to the high frequency side and a width at half height of 1.9–2.0 decades (*Figure 2*). The peak is caused by the response to the probing electric field of the polar diaryl units at the end of the side chains. At low temperatures, where the sample was in the mesophase, the loss peak was distinctly bimodal. There was a sharp low frequency δ process and a rather broader and less prominent α process visible as a shoulder on the curve to higher frequencies, as has been found with other liquid crystalline siloxane polymers of a similar structure[13–18]. It is usual to attribute the α and the δ processes to independent relaxations of the smaller transverse and larger longitudinal components, respectively, of the dipole of the polar mesogenic group[12,15,18]; the motion of the rather small dipole moment of the backbone siloxane group has not been associated with a

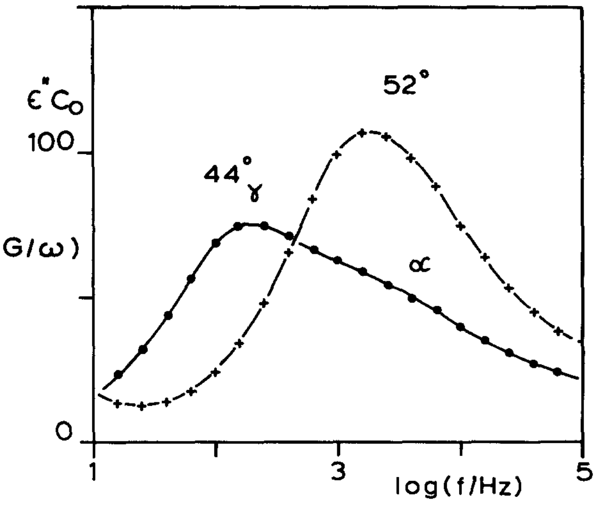

Figure 2 Dielectric loss curves for LCP6 at 44°C and at 52°C, in the nematic phase and the isotropic phase, respectively. The measurements were made using a glass cell. The curve from the mesophase shows the major peak for the δ process and the shoulder from the α process, which causes the peak to have a width of about 3.6 decades in log f. The high temperature peak has a width of 1.93 decades

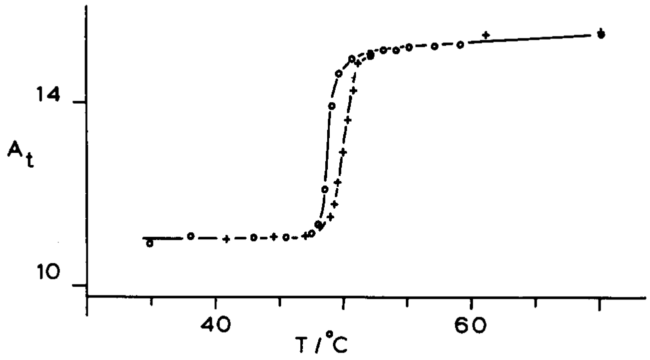

Figure 3 Plot of relative amplitude, in arbitrary units, of the dielectric loss peaks measured during cooling, ○, and during heating, +, showing an apparent hysteresis in the biphasic region

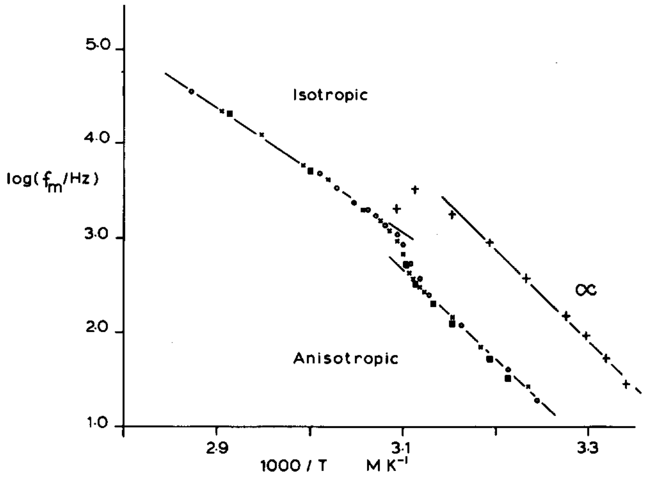

Figure 4 Arrhenius plots of log f_m against 1000/T for LCP6: ○, values obtained during the cooling process; ×, values obtained during the heating cycle; +, values obtained when heating the planar aligned sample III, which corresponds to the pure alpha process (see *Figure 7*); ■, values obtained from the crosslinked sample in the glass cell, which apparently corresponds to the pure δ process (see *Figure 8*). The values measured when cooling ○, and heating +, display a systematic divergence in the biphasic region, which is one characteristic of the apparent hysteresis also displayed by the amplitude of *Figure 3*

dielectric dispersion[14,15]. The width at half height of the envelope for the two processes was consequently ~2.6 decades; see *Figure 2*. From each of the plots of loss *versus* frequency, two parameters were obtained: the frequency of maximum loss, f_m, and the amplitude of the maximum, A_m. As has been observed with other similar polymers[12,15–17], the amplitude was noticeably lower in the mesophase than in the isotopic phase (*Figure 2*) as a consequence of the greater dispersion of the response times of the variously aligned dipole components in the former. Although the loss curves obtained from the sample outside the biphasic region were reproducible and independent of whether they were obtained during the heating or cooling cycle, there was an apparent hysteresis in the biphasic region near 50°C. The amplitude of the peaks from, for example, the loss curves obtained during the cooling cycle differed from those obtained during the subsequent heating cycle (see *Figure 3*) (each measurement was performed after a delay of 10 min for temperature equilibration throughout the brass cell and sample). A hysteresis was also seen in the plot of log(f_m) against reciprocal temperature, as is shown in *Figure 4*. The lag in frequency of the response when heating corresponds at most to a factor of two over the frequency of the process that is seen when the temperature was falling.

The stability of the hysteresis loop was examined by two isothermal dielectric studies made at 49.2°C, the temperature at which the vertical space between the amplitude curves was close to a maximum. The sample was first held at 62°C for 20 min and then quickly cooled to 49.7°C. After cooling the sample from 49.7 to 49.2°C, records of the dielectric behaviour were made over 1 d as the loss curve gradually modified to show more distinctly the α and δ processes. Upon warming the sample from below 40 to 49.2°C over a period of 3 h, and then holding the temperature at 49.2°C, the loss curve responded more quickly by changing shape in the converse direction, and achieved an equilibrium value for the amplitude within 1 d. The decay of the amplitude measured at 100 kHz while cooling was approximately exponential, with a first order decay constant of $1.57 \times 10^{-3}\,\mathrm{min}^{-1}$ ($t_{1/2} \approx 7.3$ h). The annealing initiated by warming was least squares fitted by a numerical method[20] with the following 'stretched exponential' function, which relates amplitude A_t at time t to the decay constant k:

$$A_t = A_\infty + \Delta A \times \exp[-(kt)^p] \qquad (1)$$

since the simple exponential function (equation (1), with $p = 1$) was found to be inappropriate. Here A_∞ is amplitude at infinite time. The standard deviation of the fit was thereby much improved and a value of the exponent $p \approx 0.24$ thus obtained (see *Table 1*). A smaller improvement in the fit was obtained by fitting this expression to the cooling curve data rather than using the simple exponential decay (equation (1), with $p = 1$). The magnitude of the two decays was almost the same: the equilibrium point at 49.2°C lay ~55% down from the cooling curve towards the warming curve.

In having a hysteresis of dielectric response in the biphasic region, this sample thus differs from the sample of the same polymer that had not been subjected to repeated precipitations[13,14] and from the mesogenic polysiloxane for which there were five methylene groups in the spacer[15]. It is simplest to associate the time-dependent behaviour with the sample purity: there is little impurity in the present sample to plasticize the phase changes.

Transmission measurements and planar alignment

The isotropic phase of the liquid crystalline polymer sample transmitted light more effectively than the nematic phase. Above the clearing temperature, the transmission

Table 1 Characteristics of the isothermal changes in polymer behaviour

	10^3k (min^{-1})	$t_{1/2}$ (min)	p	St. dev.[a] (%)
Decay of dielectric loss at	1.57	440	1	3.6
1 kHz after cooling to 49.2°C	0.89		0.74	1.6
Growth in dielectric loss	59	12	1	12.3
at 1 kHz after heating to 49.2°C	22		0.24	2.6
Fall in optical transmission	11.7	59	1	0.40
on cooling at 49.4°C during alignment I	12.5		1.08	0.37

[a] Standard deviation of the fit as a percentage of the change of signal over the decay. Equation (1) was fitted with a NAG routine[20]

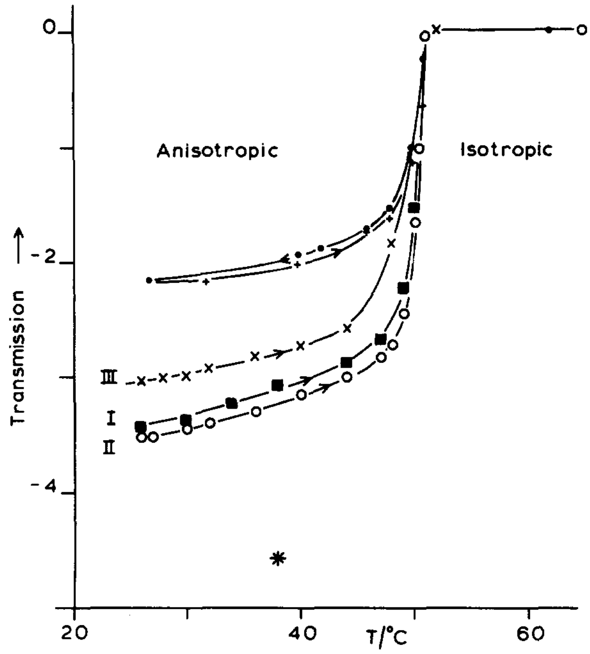

Figure 5 Plots of optical transmission, T, in arbitrary units, against temperature: ●, measurements made with one cell containing the LCP6 sample during cooling; +, measurements made during the subsequent warming. The other three curves were made with a second, more completely filled cell when warming the sample after the I, II and III alignments, as labelled. The ✱ indicates the transmission of the same sample at a single temperature when unaligned, and indicates that the sample is less opaque when planar aligned

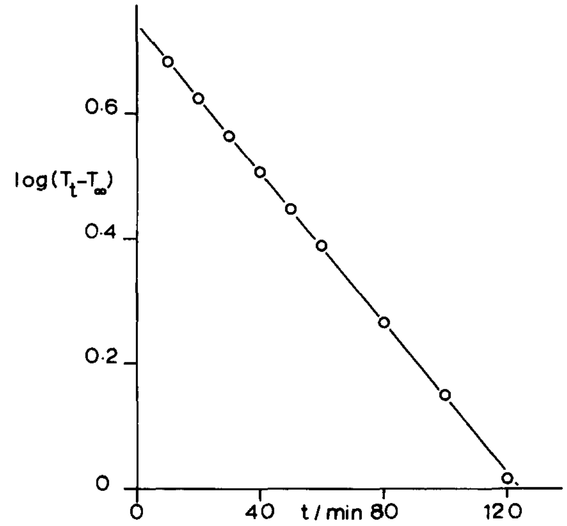

Figure 6 Logarithmic plot of the fall in optical transmission, T, of the sample during alignment I at 49.4°C, with an applied voltage of 45 V at 600 Hz. T was measured by the deflection in cm of the trace recorded on the chart paper

was independent of temperature, but below the biphasic region the transmission depended upon the temperature reversibly, as may be seen in the upper two curves of *Figure 5*. When the water bath had been adjusted to a new temperature, steady values of transmission were more readily achieved when warming than when cooling, but the time scale also depended upon the proximity to the biphasic region. Thus the transmission became constant within 12 min when warming aligned sample I by 2°C to 38°C, but 50 min were needed when warming the sample by 1°C to 50°C, most (90%) of the change taking place in the initial 10 min.

We found it convenient to monitor the optical transmission of the sample in a glass cell while attempting to align the sample by cooling it through the biphasic region in the manner used before[11,13,16–19]. Conditions that succeeded in homeotropically aligning the sample of the polymer that had not been so carefully purified ($V = 45$ V/25 μm, 600 Hz, Reference 13) were unsuccessful when the sample was cooled over 20 min from 50.0 to 47.8°C, because at that frequency the homeotropically and planar aligned phases of the present sample probably have similar dielectric constants. (It is the difference in dielectric constants between the two types of aligned sample that provides the driving force for aligning all the microregions of the mesophase as they form from the isotropic phase in a direction determined by that of the field.)

Planar alignment (I) was obtained by cooling the sample much more slowly under the influence of the 600 Hz field. The rate of cooling during this alignment was carefully controlled down to 49.4°C, when the transmission started to fall, and the temperature was then kept constant for >6 h. The transmission of the sample fell exponentially (see *Figure 6*), with a decay constant of $1.2 \times 10^{-2}\,\text{min}^{-1}$ ($t_{1/2} = 59$ min). Note that the rate of approach to the equilibrium organization of the liquid crystalline polymer, measured optically at 49.4°C when an aligning electric field prevailed, was an order of magnitude higher than that of the rate measured dielectrically at 49.2°C for the process that took place in the absence of an electric field (see *Table 1*). If the slight difference of temperature is neglected, it appears that the electric field can promote or accelerate the growth of mesophase. (The field from the bridge during dielectric measurements was only 1–0.5 V, and was effective only when the intermittent measurements were made.)

As well as this alignment at 600 Hz, planar alignment was also obtained at higher frequencies, where the dielectric constants of the two aligned phases differ more. One experiment (III) that used an electric field of 50 V across the 25 μm thick sample and a frequency of 5 kHz was the most successful, as judged by the virtual absence of the δ process from the loss plot (see *Figure 7*). For this alignment the temperature was slowly lowered to 49.2°C, where it was held until the transmission of the sample was seen to fall. The temperature was lowered over a period of 130 min to maintain an approximately constant rate of fall of the transmission until the temperature reached 48.2°C, when the temperature was lowered more quickly down to 25°C. The loss in transmission that took place on each alignment was less than that which occurred when no alignment was achieved, though the naive expectation that the planar aligned liquid crystalline polymer might be as transparent as the isotropic phase was not confirmed. While the best aligned sample was the least opaque, two other alignment experiments had different orders for alignment as measured by transparency (III > I > II*; see *Figure 7*) and by the magnitude of the remnant of the δ process seen in the loss plots (III > II > I).

Upon warming, the optical transmission of each of the aligned samples rose steadily until the biphasic region was reached, whereupon the transmission rose more steeply to the isotropic value, much as had the earlier

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* Alignment II was performed by cooling the sample slowly through the biphasic region with a field voltage of 45 V at 10 kHz

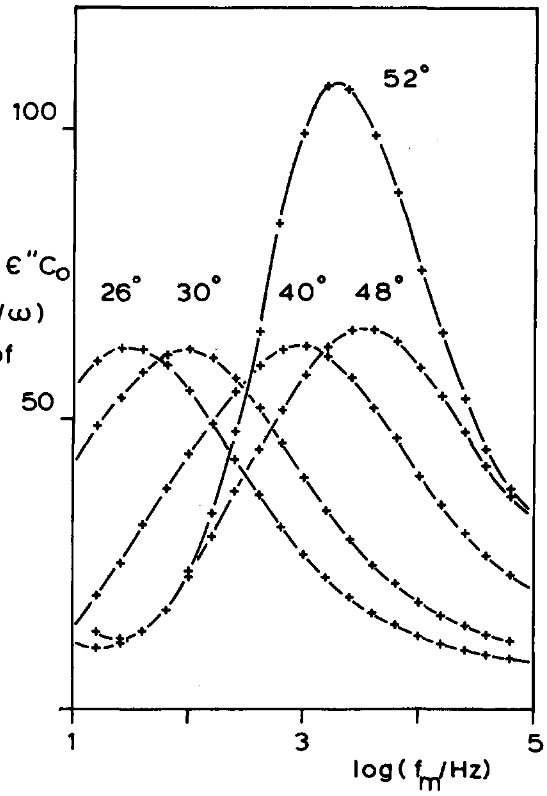

Figure 7 Dielectric loss curves for planar aligned LCP6 (after alignment III) recorded at stages when warming the sample to the isotropic phase and during the measurement of the light transmission curve of *Figure 5*. At low temperatures the curve is nearly symmetrical and shows no visible indication of the presence of the δ process on the low frequency side of the main peak, e.g. at 40°C the δ peak would be seen in the unaligned liquid crystalline phase at $\log f_m \approx 1.75$

non-aligned sample, as is shown in *Figure 3*. The changes were associated with changes to the texture of the liquid crystalline phase. The dielectric loss peak of the α process evident in this aligned sample (III) had a width at half height of about 2.9 decades in $\log f_m$ (see *Figure 7*), which is a little higher than the value of 2.5 decades found for the polymer that had not been reprecipitated as often[13]. The increase in width of the loss peak on removal of contaminant indicates that the α process is now even more cooperative in character. The loss curve was measured at several temperatures during warming and alignment was maintained (see *Figure 7*) until, within the biphasic region, the amplitude of the loss rose substantially as the α process of the anisotropic phase was transformed into the isotropic relaxation. While traversing the biphasic region towards isotropy in a manner non-reversible in the absence of an aligning field, the value of f_m fell, revealing an apparent negative activation energy for the loss process. This reflected the increasing activity of the δ relaxation as the $\mu_{\parallel}$ dipole components of the polar units became more randomly oriented.

Studies on gelled liquid crystalline polysiloxane

On one occasion, after the siloxane polymer was placed in the brass cell and this was heated at 150°C for 15 h under vacuum to remove dissolved gasses, we found anomalous dielectric behaviour. A second sample of the polymer also showed the new behaviour after it had been heated at 120°C for $\approx$4 d while filling a glass cell by gravity. After removing the sample from the brass cell, it appeared to have changed little. After slow cooling through the biphasic region, the sample in the glass cell showed a conic plane texture that extended over a space of 5 mm, and its clearing temperature, recorded with a hot-stage microscope as 51°C, was little changed by the crosslinking. When placed in a solvent such as dichloromethane it merely swelled in the manner of a gel, rather than dispersed as did the normal polymer. Though remaining a liquid crystal, the sample had apparently crosslinked, perhaps by a reaction involving unused Si–H bonds and the nitrile groups[12]. Statistically, only one residue per molecule, about 3% of all the residues, need be involved for the mass to become crosslinked[21], so the extent of any chemical change may be slight, but the consequences for the dynamics of the mesogenic groups are apparently profound.

The loss curves for the crosslinked samples were recorded at temperatures above and below the clearing temperature (see *Figure 8* for some of these). Three points can be made about these curves. First they appeared to be much smaller in magnitude than the curves obtained from the normal polymer. The amplitude values displayed by the curves in *Figure 8* are about half the values shown in the plot of *Figure 3*, whose values were also obtained from a sample of the normal polymer in the same brass cell. Crosslinking has restricted the response of the dipoles to the measuring electric field. Second, the curves obtained from the mesophase were found to be almost entirely lacking in the α relaxation: that response by the polar units does not take place. Third, it may be seen in *Figure 8*, where measurements made on the sample that crosslinked in the brass cell are shown, that the amplitude of the loss peak has quite constant values on each side of the biphasic region, but falls by about 10% as the temperature is raised through the biphasic region, which contrasts with the behaviour of the normal polymer.

The absence of the α process reveals that the width at half height of the pure δ process is 1.9 decades of frequency, which is about the same as was found for another polymer containing the same mesogenic group[14]. The drop in peak amplitude over the biphasic region is accompanied by a rise in peak width, so that the

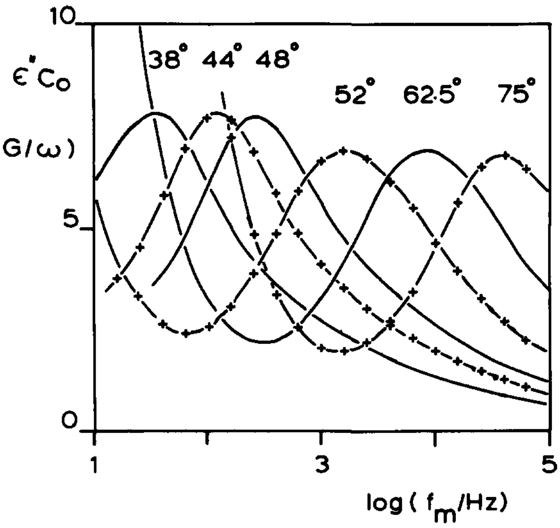

Figure 8 Loss curves measured on the sample that had gelled in the brass cell, showing how the δ process is absent at low temperatures from its normal position (compare the plot for 44°C with that shown in *Figure 2*), and how the amplitude drops at the clearing point

magnitude of the dipole response is hardly altered. The shapes of the dielectric curves obtained from the gel were not as reproducible as they were for the normal polymer if large excursions from a particular measurement temperature were made. This may be because the sample is a gel, with an elaborate network structure. The magnitude of the step in amplitude was reduced to ~4% for the same sample after it had been annealed at 90°C for 4 h, and similarly was smaller for the sample that had crosslinked in the glass cell. Below the clearing temperature the values of f_m for the gel were ~12% below the values measured on an unaligned sample, but above the clearing temperature the values of f_m differed little from the values found for the normal polymer, as is shown on the Arrhenius plot of *Figure 4* (not all the measurements of f_m are shown (as squares) because some coincided exactly with the points for the normal polymer). The small shift in measured f_m below the clearing temperature is attributable to the absence of a perturbation to the shape of the peak from the α relaxation.

The anomalous behaviour was thus characterized dielectrically by the smaller amplitude of the dielectric loss response upon gel formation, the relatively reduced activity of the α process at temperatures below the clearing temperature and the replacement of the clear step up by a step down in amplitude of the loss plot as the temperature was raised through the biphasic region.

The unexpected behaviour of the sample may have two causes: the heat treatment may have caused the sample to become homeotropically aligned on cooling within the glass and brass cells through some surface effect promoted by a reaction between the polymer and the brass and the polymer and the doped glass surfaces. Surface treatment effects are known to cause other liquid crystalline substances to become aligned[1,5], and the natural condition of a siloxane polymer studied in a brass cell similar to that used here was found to be slightly planar aligned[13]. However, such an explanation may be incompatible with the slow cooling rate required to obtain in an electric field an aligned sample of the normal polymer. Moreover, it does not address the behaviour of the material in the isotropic phase, where the amplitude of the loss is clearly less than that in the ordered phase, in clear contrast with the behaviour of the planar aligned and the unaligned sample.

Alternatively, the dynamics of the mesogenic units have been altered by the crosslinking process. While the amplitude of the dielectric losses of both the α and the δ modes of dielectric relaxation appear to be affected, it is surprising that it is the high frequency α process which is most restricted by the crosslinking reaction, for this is the most mobile process. It is notable that in the normal liquid crystal sample of this polymer the α process has a greater width than the δ process, suggesting that the former process is more cooperative in character in the sense that a greater number of dipoles and a more extensive volume of the mesophase is concerned in the relaxation. If that is the case, the relaxation may be more susceptible to a new constraint on motion created within the liquid crystalline matrix by the formation of the crosslinks between the polymer backbones. An alternative view would suggest that the α process is coupled in some way to the chain dipole relaxation, and so is restricted when the main chain motions are constrained by the crosslinks.

Activation energies for the relaxation processes

For the unaligned polymer the slopes of the two linear portions of the Arrhenius plot, which are shown in *Figure 4*, provided the following activation energies for the dielectric relaxation: isotropic region, 127 (±3) $\mathrm{kJ\,mol^{-1}}$; anisotropic region, 182 (±3). The corresponding values for the less pure sample of the polymer were found to be 139 (±5) and 195 (±5) $\mathrm{kJ\,mol^{-1}}$ (Reference 14), which are surprisingly a little higher than the present values. We might have expected impurities to facilitate the relaxation processes. The isotropic process for the polymer with a polymer having a five methylene group spacer had an activation energy of 183 $\mathrm{kJ\,mol^{-1}}$ (Reference 15), which is not significantly different from the value for the present polymer. The Arrhenius plot of the measured f_m of the α process within the aligned sample is also shown on *Figure 4*, and outside the biphasic region provided an activation energy of 187 (±5) $\mathrm{kJ\,mol^{-1}}$. This value is not very different from that obtained for the peak in the unaligned sample, where the peak itself derives mainly from the δ relaxation. We have not obtained an activation energy for the δ process shown by the gelled sample, but it is clear from the position of the points on *Figure 4* that neither the activation energy nor the frequency of the δ process would differ much from the value found for the unaligned material. The not too stringently purified mesogenic polysiloxanes, which had an eight methylene spacer group, had activation energies of ~120 $\mathrm{kJ\,mol^{-1}}$ for the α and δ processes at 60°C (Reference 16).

The activation energies thus depend more upon whether the polar unit is in a mesophase or in the isotropic phase than upon the length of the spacer, and hardly at all on whether the polymer is linear or has gelled. The last observation, together with the observation that gelling has cut out the α relaxation, is not understood, for in general in passing from a small to a polymeric mesogen rates of motion fall and activation energies rise significantly[22].

CONCLUSIONS

The high purity of the polymer studied here is associated with the appearance of a hysteresis effect in the biphasic region. The sample has been successfully planar aligned. On cooling to the biphasic region the formation of mesophase is probably accelerated by an aligning field. The activation energies for motion of the dipolar side chain units do not differ much from the value found for similar polymers with slightly different structures, but a crosslinking reaction of the polymer has caused profound changes in the dynamics of the mesogenic groups, though the material remained a liquid crystal. The high frequency α relaxation was apparently removed from the dielectric spectrum upon the creation of crosslinks.

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