# Experimental observation of a novel phenomenon in the biphasic region of a nematogenic siloxane polymer: the recovery of homeotropic alignment in the absence of external fields

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It is shown that cooling a partially homeotropically aligned liquid crystalline siloxane polymer from the biphasic region into the liquid crystalline (l.c.) region leads to homeotropic alignment of the phase in the absence of a directing electric field. Partially aligned samples were prepared either by heating a homeotropic sample into the biphasic range or by cooling an isotropic sample into the biphasic range in the presence of an a.c. directing electric field. The alignment recovery was monitored using wide frequency dielectric relaxation spectroscopy. The extent of recovery was dependent on the cooling rate and on the number of thermal cycles made to fixed temperatures in the biphasic and l.c. states. The origin of the recovery process is assigned to a 'template crystallization' of molecules on pre-existing aligned l.c. phase, and its relevance to the formation of aligned l.c. polymer material in applied a.c. electric fields is discussed.

**(Keywords: liquid crystalline polymer; electric field alignment; alignment recovery; template recrystallization)**

## INTRODUCTION

Oligomers and linear polymers having side chains containing highly anisometric groups form liquid crystalline phases whose properties are hybrid between those of the parent polymer and those of low molar mass liquid crystals. This combination of properties arises since the anisometric groups in the side chains promote mesophase formation while the polymer backbone tends to promote the formation of liquid or glassy phases[1-5]. Such polymers may be aligned macroscopically using combinations of thermal and electrical treatments[4-10], or thermal and magnetic treatments[11] or by direct application of an a.c. electric field to the liquid crystal material at a fixed temperature[6,12,13]. Most studies using aligning electric fields report the formation of homeotropically aligned material[4-10], but it is possible to obtain planarly aligned material using high frequency electric fields[10,14] or by a steady magnetic field[11]. In common with low molar mass smectic materials, but in contrast with low molar mass nematic materials, polymeric liquid crystals form mesophases which, once macroscopically aligned, may retain the alignment both above and below the apparent glass transition temperature $T_g$ of the material. Macroscopic alignment is destroyed, together with the molecular long-range orientational order, by heating the material into the isotropic phase[4,7,14]. The differences in optical texture between the homeotropically aligned and unaligned materials form the basis for the proposed use of liquid crystalline side-chain polymers in field-assisted thermal erase/write (FATE/W) optical information storage systems[5,6,15,16]. The ability to perform repeated and well defined FATE/W operations on thin films (1–25 $\mu$m) of the mesogenic polymers, coupled with the fact that the optical refractive indexes $n_\parallel$ and $n_\perp$ for a monodomain are significantly different, suggests that such materials could be used as optical elements having microstructure (e.g. Fresnel lenses[17]) or as planar waveguides in reconfigurable optical computing systems. Also, their use as host systems containing guest molecules with high optical hyperpolarizabilities is currently being explored[18,19].

The realization of much of the technological potential of the liquid crystalline side-chain polymers depends on the ability to prepare films with precisely controlled macroscopic alignment. Therefore a sound understanding of the experimental and theoretical factors that affect the formation of aligned materials is essential in their present and proposed applications.

We have demonstrated that dielectric relaxation spectroscopy provides a direct non-optical method for monitoring the nature and extent of macroscopic alignment in certain nematic and smectic siloxane polymers[7-10,12-14,20]. From these studies we have concluded that an efficient method of obtaining a macroscopically aligned mesophase for a polymeric material is to cool slowly from the isotropic phase in the presence of a directing a.c. electric field, the nature and

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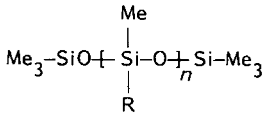
extent of alignment being determined by the cooling rate and by the amplitude and frequency of the directing field, as indicated above. In particular, we found that alignment processes occur in the biphasic range (i.e. the range in which the liquid crystalline phase and isotropic phase coexist in thermodynamic equilibrium) as the sample is cooled. The nature of the alignment process in this range is the subject of this paper. Our results provide experimental evidence for a remarkable phenomenon associated with the biphasic range, one which promotes the formation of a macroscopically aligned mesophase even in the absence of the directing electric field. The implications of these observations for the mechanism of formation of aligned material and for the applications that involve FATE/W processes will be briefly discussed.

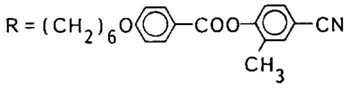
## EXPERIMENTAL RESULTS AND DISCUSSION

The material chosen for this study is a siloxane homopolymer which has been the subject of extensive dielectric studies[7–11,13,14,20] and which has the following structure



$$\mathrm{Me_3{-}SiO{+}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle Me}{|}}{Si}}{-}O{+}_{n}Si{-}Me_3}$$

where $n = 50$ and



This material was provided by Professor Gray and Dr D. Lacey of Hull University, UK.

It is nematogenic, and differential scanning calorimetry (d.s.c.) data indicate that the onset of the biphasic region occurs at ≈314 K ($=T_N$) and extends until ≈319 K ($=T_I$). Our dielectric data corroborate these values[10,14]. The sample was prepared as a disc (120 $\mu$m thick, 1.0 cm in diameter) sandwiched between two polished brass electrodes. Constant sample dimensions were maintained by means of a PTFE gasket. The electrodes were housed in a three-terminal cell as described previously[21]. The cell was immersed in a thermostatted water bath and temperature stability at the sample was estimated to be better than ±0.02 K. Dielectric data were acquired by means of an automated system based on a GenRad 1689 Digibridge.

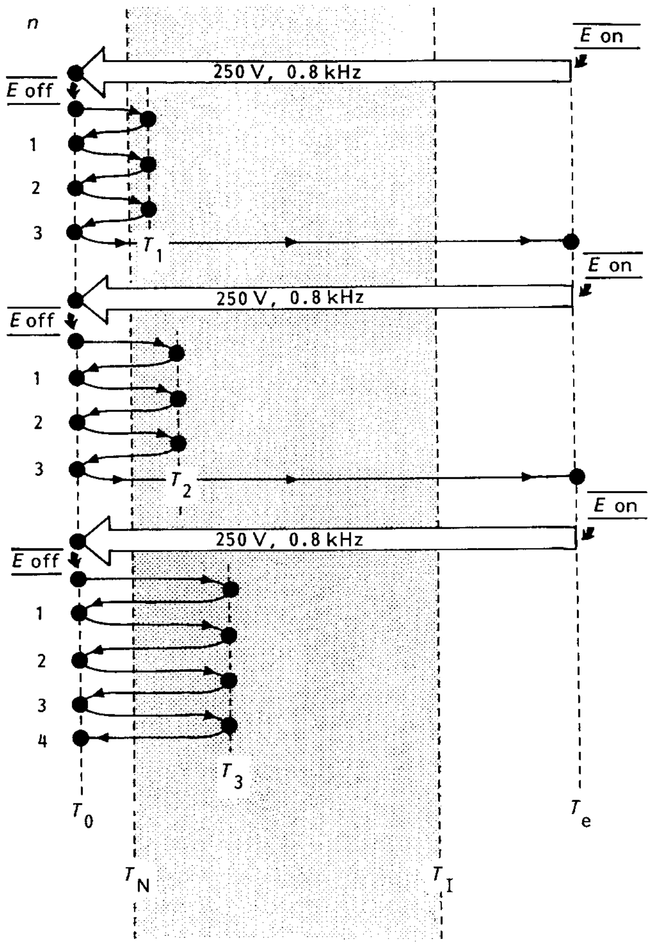


**Figure 1** Schematic plan of the experiment. $T_0$, the measuring temperature, is 312.2 K. $T_e$, the erasing temperature, is 328.0 K. $T_1$ (=314.9 K), $T_2$ (=315.4 K) and $T_3$ (=315.9 K) are the recycling temperatures in the biphasic region

A schematic plan of the experiment is illustrated in *Figure 1*. The sample was heated to a temperature $T_e$ (=328.0 K), at which it was fully isotropic. The dielectric loss spectrum was recorded at this temperature. A directing electric field at 250 V r.m.s. at 0.8 kHz frequency was applied to the sample, which was then cooled at a rate of ≈0.1 K min$^{-1}$ to a temperature $T_0$ (=312.2 K) at which the sample was nematic. Previous work had shown that a fully aligned homeotropic material is obtained under these conditions[10,14]. The directing field was removed, the sample was short-circuited to remove extraneous transient effects, and a loss spectrum was recorded at this reference temperature $T_0$. The fully aligned material was then heated to a temperature $T_1$ (=314.9 K) just above $T_N$. By continuously monitoring the capacitance and loss at a chosen frequency (10 kHz) we were able to follow the changes which occur as the material becomes biphasic and equilibrates at $T_1$. Equilibration times of 5–7 min were obtained, measured from the time at which the water bath attained the pre-set temperature $T_1$. We found that following equilibration, the dielectric properties of the material remained unchanged with time even for periods up to 4 h, irrespective of the reference temperature in the biphasic range ($T_1$, $T_2$ etc.) at which the dielectric measurements were made. When thermal equilibrium was established at $T_1$, a loss spectrum was recorded. The bath temperature was decreased to $T_0$ (=312.2 K) in 0.1 K intervals with an effective sample cooling rate (excluding measurements) of 0.1 K min$^{-1}$. Loss spectra were recorded at several temperatures during the cooling process by holding the bath temperature at a chosen value, and making measurements at that temperature following equilibration. Having reached $T_0$, the loss spectrum was again recorded and the film was reheated to $T_1$. The loss spectrum was recorded at $T_1$ and the cooling cycle, together with measurement of loss spectra at the same temperatures as before, was repeated until $T_0$ was again reached. The heat–cool cycles were repeated and further loss data were obtained. Care was taken to ensure that the duration of the cooling cycle, the timing of the different cooling intervals and the measurement times faithfully repeated those established by the first cooling. The sample was cycled from $T_0$ through $T_1$ three times. The aim of this, and the subsequent experiments, was to monitor the changes in dielectric properties, as a fully aligned sample is heated from a temperature $T_0$ in its nematic state to a reference temperature ($T_1$ as described above) in the biphasic range, then cooled slowly back to $T_0$ and the process repeated several times.

Following the thermal cycle $T_0 \rightarrow T_1 \rightarrow T_0$, the film was heated into the isotropic state at $T_e = 328$ K in order to erase any residual homeotropic alignment. It was then cooled to $T_0 = 312.2$ K in the presence of the aligning field, as before, to produce a fully homeotropic film. This material was heated to $T_2 = 315.4$ K in the biphasic range and the thermal cycles, with measurement of loss spectra, were repeated. The sample was cycled three times through $T_2$. Similarly, a homeotropic sample was cycled four times from $T_0 = 312.2$ K through $T_3 = 315.9$ K. Note that the loss spectra for all homeotropic films at $T_0$ and isotropic films at $T_e$ were found to be reproduced accurately, showing that the sample geometry remained unchanged during these studies.

*Figure 2* shows representative loss data for samples at $T_0$ following cooling from $T_1$, $T_2$ and $T_3$ to $T_0$ (after three coolings in each case). Also shown are the loss curves for the fully aligned homeotropic and non-aligned materials at $T_0$. Here $G/\omega = \varepsilon'' C_a$, where $G$ is the equivalent parallel conductance of the sample at the angular frequency $\omega$, $C_a$ is the interelectrode capacitance and $\varepsilon''$ is the dielectric loss factor of the sample. We see that on going from the non-aligned to the fully aligned material there is a marked increase in the maximum loss factor and a shift of the frequency of maximum loss to lower values. Such behaviour has been described and analysed in an earlier paper[20].

The curve for the homeotropic material has a width at half-height of 1.3 units of $\log_{10}\nu$, which is only slightly greater than that for a single relaxation time process (1.14). In contrast, the curve for the non-aligned material is very broad and asymmetric. The loss curves obtained after the different heat–cool cycles are intermediate between those for the homeotropic and unaligned materials. Their extent of alignment may be estimated qualitatively in terms of the ratio $R/R_0$ where $R$ is the value of maximum loss factor for the sample of intermediate alignment and $R_0$ is the corresponding quantity for the non-aligned material, both obtained at $T = T_0$. Values of $R/R_0$ are shown in *Figure 3*. The filled circles are for the fully homeotropic material during its first heating cycle from $T = T_0$.

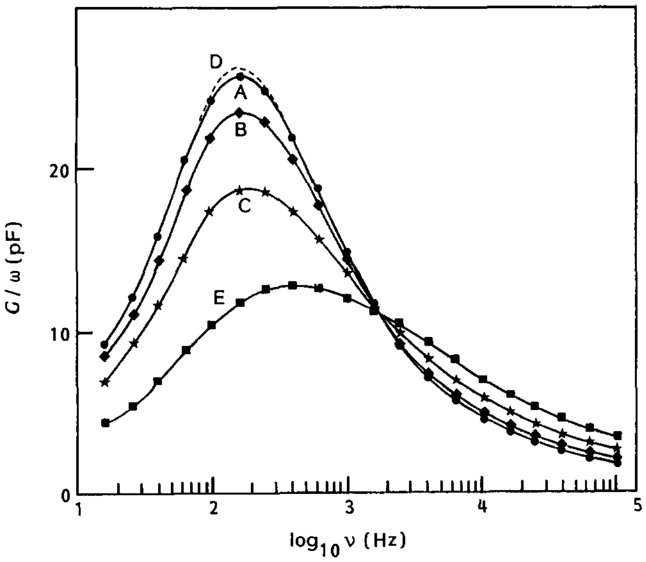


**Figure 2** Representative examples of dielectric loss curves obtained after thermal cycling through the biphasic region for samples at 312.2 K. A, Third cooling cycle from $T_1$; B, third cooling cycle from $T_2$; C, third cooling cycle from $T_3$. D and E denote, respectively, the loss curves for the homeotropic and non-aligned samples

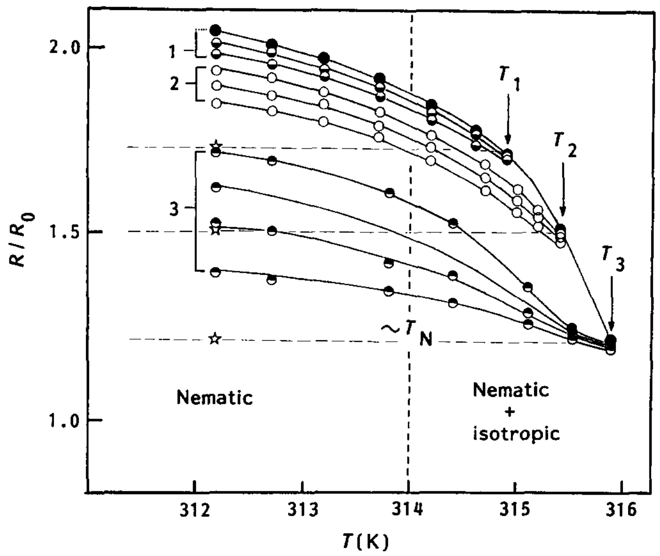


**Figure 3** Plot of the scaled amplitudes of maximum loss as a function of temperature. The curves shown were obtained by thermal cycling of the initially homeotropic phase through (1) $T_1$, (2) $T_2$ and (3) $T_3$. The stars denote the values of $R/R_0$ for the material shock-cooled from the three temperatures in the biphasic

Consider a sample which is fully homeotropic at $T = T_0$ and which is heated to a temperature $T_i$ in the biphasic range. At $T = T_i$ the nematic component will have the same alignment as that in the original material at $T_0$. When this biphasic material is cooled back to $T_0$ in the absence of the applied field, the isotropic component will reform the nematic liquid crystalline (l.c.) phase so at $T = T_0$ the material is fully nematic. If the l.c. component reforms with no orientational correlation with the aligned nematic phase which is present, then at $T = T_0$ the material would be partially aligned, comprising $x$ (wt fraction) of aligned l.c. phase and $(1-x)$ of non-aligned l.c. phase. Should the aligned l.c. component in the biphasic material at $T = T_i$ exert a directing influence on the mesophase formed by the isotropic component on cooling then some enhanced alignment of the reformed l.c. phase at $T = T_0$ may occur. If this directing influence was present then the homeotropic material would be partly reconstituted at $T_0$ on cooling from $T_i$, and this would be reflected in the dielectric loss spectrum, such that $R/R_0$ would be intermediate between that for the fully homeotropic and unaligned materials. The lower limit for $R/R_0$ at $T = T_0$ was determined by heating the fully homeotropic material to $T = T_i$ and then shock-cooling in the absence of an applied field to $T = T_0$ and recording the dielectric spectrum at $T_0$. Under these conditions the isotropic phase forms unaligned l.c. phase. The range of $R/R_0$ was found to be $2.05 > R/R_0 > 1.75$, 1.52, 1.23 for $T_i = T_1$, $T_2$ and $T_3$, respectively.

By comparing the curves in *Figure 3* for the first cooling cycle from the three temperatures $T_i$ we find that in each case the isotropic component forms the nematic phase on cooling, which has an enhanced homeotropic alignment as evidenced by the fact that at $T_0$ the ratio $(R/R_0) > (R/R_0)_{\text{shock}}$. It should be stressed that this alignment is induced in the absence of external electric or magnetic fields or of surface forces.

The extent of homeotropic alignment decreases the higher in the biphasic is the recycling temperature $T_i$. This observation suggests that the homeotropic nematic component is responsible for breaking the symmetry of the system, in a manner analogous to that of a magnetic or electric field. The inverse relation between the extent of alignment and $T_i$ is due to the decreasing volume fraction of nematic component as $T_i \rightarrow T_{iso}$. Alternatively, the homeotropic component of the biphasic material could be acting as a 'template' for the ordered formation of a further nematic phase by a nucleated process analogous to epitaxial growth on a crystal surface. Further thermal cycles result in a decreasing extent of alignment, indicating that the effect is related to the average degree of homeotropic alignment of the sample as a whole.

Since the volume fractions $x$ and $(1-x)$ of the two coexisting phases are determined by the temperature $T_i$ we expect that the biphasic material obtained by heating a fully homeotropic material to $T_i$ should be indistinguishable from a biphasic material obtained by cooling a sample from the isotropic phase to $T_i$ in the presence of a directing electric field. In both cases the biphasic material consists of $x$ homeotropic nematic phase and $1-x$ isotropic phase. Accordingly, further cooling, in the absence of a directing field, of the biphasic material prepared by slow cooling from the isotropic phase in an applied field should result in the 'template-induced' alignment described previously. The experimental sequence designed to confirm this is indicated in *Figure 4*. The results we obtained from this second set of experiments are shown in *Figure 5*. Homeotropic realignment in the $1-x$ volume fraction is observed as in the first set of experiments, showing that the aligned nematic component does indeed induce the formation of further homeotropic mesophase as $T \rightarrow T_0$. However, it is interesting to note that the extent of homeotropic alignment in this set of experiments is more pronounced than in the previous set (*Figure 3*). For example, the material prepared by heating from $T_0$ to $T_2$ and then cooling to $T_0$ was characterized by $R/R_0 = 1.9$ at $T_0$, whereas the material prepared by cooling the isotropic phase to $T_2$ in the presence of a directing electric field and then subsequently cooling to $T_0$ in the absence of the field gave $R/R_0 = 2.05$ at $T_0$, indicating the formation of an essentially completely aligned film. This behaviour seems to become less pronounced as $T_i \rightarrow T_I$ and for $T = T_3$ the extent of alignment induced in the $1-x$ volume fraction is the same in both sets of experiments. As yet we are unable to account for this interesting asymmetry, except to say that the material has a memory of the different thermal/electrical treatments used to produce it.

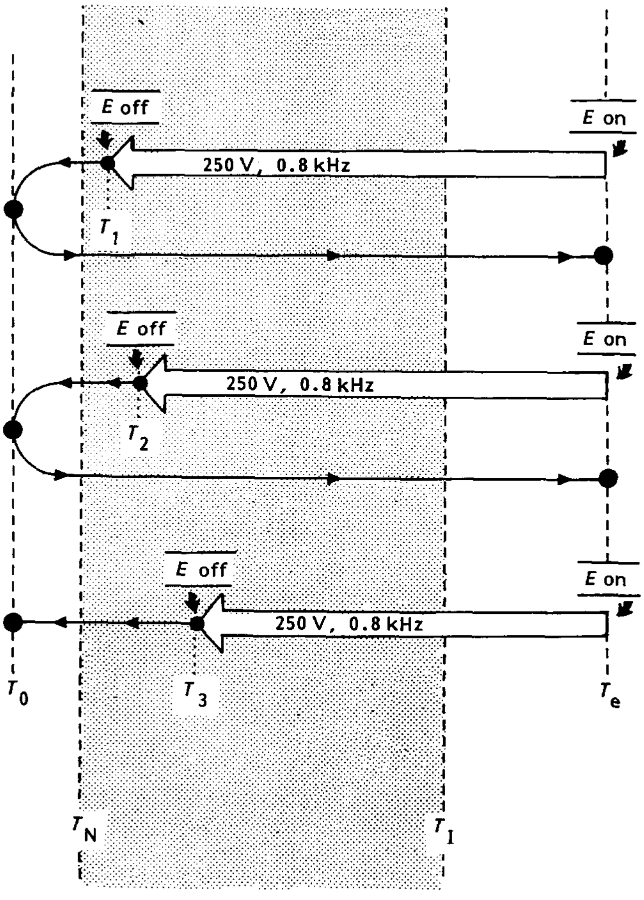


**Figure 4** Schematic plan of the second set of experiments, complementary to those shown in *Figure 1*

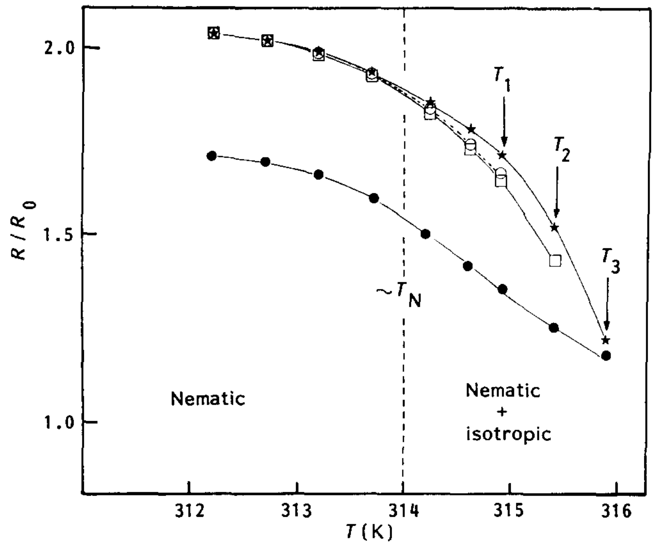


**Figure 5** Plot of the scaled amplitudes of maximum loss as a function of temperature for an isotropic sample cooled to $T_i$ in the biphasic in the presence of an a.c. electric field (250 V rms, 0.8 kHz) and subsequently cooled in the absence of the field as indicated in *Figure 4*. ●, □ and ○ correspond to cooling from $T_3$, $T_2$ and $T_1$, respectively. Δ corresponds to heating from $T_0$

So far our discussion of the experimental data has been based on the observation that the quantity $R/R_0$ reflects the degree and nature of macroscopic alignment. To show that the relationship between $R/R_0$ and the degree of order is not a simple one it is necessary to consider in greater detail the dielectric loss curves we obtained.

In earlier publications[20,22] we have shown that, provided we assume that the measuring electric field is uniform in the sample, the complex permittivity can be written as

$$\varepsilon_z = \varepsilon_\infty + \frac{G}{3kT}\left[\frac{(1+2S_d)}{3}\{\mu_e^2(1+2S)F_\parallel^l(\omega) + \mu_t^2(1-S)F_\parallel^t(\omega)\} + \tfrac{2}{3}(1-S_d)\{\mu_e^2(1-S)F_\perp^l(\omega) + 2\mu_t^2(1+\tfrac{1}{2}S)F_\perp^t(\omega)\}\right] \quad (1)$$

where $S$ is the local order parameter and $S_d$ is a 'director order parameter' that represents the degree of macroscopic alignment of the local directors ($-0.5 \leqslant S_d \leqslant 1$).

According to this equation there are four relaxation modes, two involving motion of the *longitudinal* component $\mu_e$ of the dipole moment of the mesogenic head group, which are characterized by the relaxation function $F^l_{\parallel}(\omega)$ and $F^l_{\perp}(\omega)$, and two involving motion of the *transverse* component $\mu_t$ of the dipole moment of the mesogenic head group, which are characterized by the relaxation functions $F^t_{\parallel}(\omega)$ and $F^t_{\perp}(\omega)$. The complex permittivity is given by $\varepsilon_Z(\omega) = \varepsilon'_Z(\omega) - i\varepsilon''_Z(\omega)$, so the loss curves give information on the imaginary parts of the relaxation functions $F^i_j(\omega)$, suitably weighted by $S_d$. The loss curves shown in *Figure 2* are featureless, showing that all four relaxation modes are closely spaced in the fequency domain. As a result it is not possible to resolve the curves shown in the figure into their *four* component curves. As has been shown in earlier publications[9,22] such composite curves can be resolved into two component curves labelled $\delta$ and $\alpha$ in ascending order of frequency. The total integrated intensities (i.e. the amplitude of maximum loss × $\Delta\frac{1}{2}$) for these curves are related to the quantities introduced in equation (1) by:

$$A_\delta = (G\mu_e^2(/kT)(1 + 2S_d + 2S + 4S_dS) \qquad (2a)$$

$$A_\alpha = (G\mu_e^2/9kT)\{2 - 2S_d - 2S + 2S_dS + 3R_\mu(1 - S_dS)\} \qquad (2b)$$

$$R_\mu = \mu_t^2/\mu_e^2$$

The curve for the $\alpha$-process is much broader than that for a single relaxation process.

From these equations it can be seen that when $S_d \simeq 1$ the total integrated intensity of the composite curve is mainly due to the $\delta$ process and for $S_d \rightarrow 0$ the $\alpha$ and $\delta$ curves both contribute to the total intensity. Thus the ratio $R/R_0$ would be proportional to $S_d$ only if the amplitudes of maximum loss of the constituent $\delta$ peaks were compared, i.e. $R^{(\delta)}/R_0^{(\delta)}$. Accordingly, we now turn out attention to the question of estimating $S_d$. Clearly, if we fit the experimental loss curves to the two Fuoss–Kirkwood component curves[22] we can use equation (2a) to determine $S_d$ from the ratio $A^{(\delta)}/A_0^{(\delta)}$. However, as we have shown recently[20], there is a simple way of obtaining accurate estimates of $S_d$ for a partially aligned specimen. If we assume that equation (1) applies to our data then the director order parameter $S_d$ can be determined using the relation[20]

$$S_d = \frac{\varepsilon''_Z(\omega) - \bar{\varepsilon}''(\omega)}{\varepsilon''_{\parallel}(\omega) - \bar{\varepsilon}''(\omega)} \qquad (3)$$

where $\bar{\varepsilon}''(\omega) = \{\varepsilon''_{\parallel}(\omega) + 2\varepsilon''_{\perp}(\omega)\}/3$ and is the loss factor at frequency $\omega$ (rad $s^{-1}$) for the non-aligned material. By comparing the loss data for a partially aligned sample with that for the fully homeotropically aligned and non-aligned samples at the same frequency ($\omega$) and the same temperature, equation (3) yields a value of $S_d$ for the unknown sample at that temperature.

*Figure 6* shows the values of $S_d$ determined for the experiments described above involving $T_0 \rightarrow T_i \rightarrow T_0$ cycles (see also *Figures 1–3*). A striking feature of these data is that $S_d$ appears to be almost an asymptotic function of the number of thermal cycles through the biphasic region. This aspect is investigated in the following paper[23].

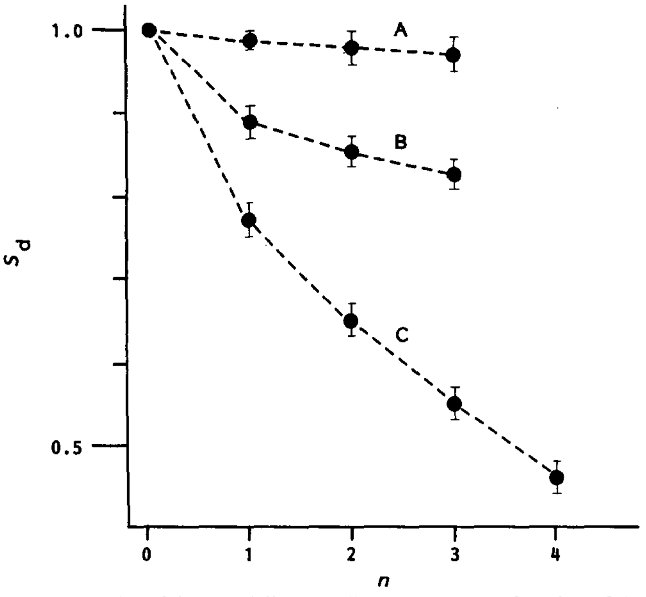


**Figure 6** Plot of degree of director alignment, $S_d$, as a function of the number of thermal cycles through the biphasic region for the three chosen temperatures: A, $T_1$; B, $T_2$; C, $T_3$

These experiments show that the liquid crystalline phase formed on cooling a biphasic material, which is partially aligned macroscopically, tends to have a strong correlation of alignment with the aligned l.c. phase. This may be understood as follows. Consider an isotropic liquid which is cooled, in the presence of a strong directing field, just into the biphasic range. The liquid crystal phase first formed consists of nuclei which propagate to form the mesophase. The nuclei will either form aligned with respect to the directing field or will reorient rapidly into the field direction. As the temperature is lowered further, propagation of aligned material on that already present will occur; new aligned nuclei will also form and propagate the aligned phase. The dominant process appears to be propagation of the mesophase on existing aligned mesophase and this will occur in the presence or absence of an applied field.

## CONCLUSIONS

We have observed a novel phenomenon in the realignment of a liquid crystalline siloxane polymer. It has been shown that if a biphasic material contains a l.c. phase which is aligned macroscopically, either by heating an aligned material into the biphasic range or cooling from the isotropic phase into the biphasic range with a directing electric field applied, then subsequent field-free slow cooling of the biphasic material leads to alignment recovery of the mesophase. The extent of alignment recovery is related to the volume fraction of mesophase present in the biphasic material, to the cooling rate used, and to the number of times the sample was cycled through the biphasic region. The implications for the formation of aligned materials on cooling from the isotropic state into the liquid crystalline state, via the biphasic range in the presence of a directing electric field, are clear. These observations are also important for technological applications of such polymers that are based on FATE/W with focused laser beams since they require thermal cycling through the biphasic region. A template-mediated phenomenon of the kind we have found in our experiments could affect the reproducibility of write/erase operations if thermal/electrical histories of sample are not controlled carefully.

A feature of this work is that it shows how dielectric relaxation studies can provide direct information on the state of alignment of materials produced by a variety of thermal/electrical histories.

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