Template-induced recovery of homeotropic alignment in the biphasic region of a nematogenic siloxane polymer: a simple phenomenological model

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A simple empirical theory is described which models the partial melting behaviour of a homeotropically aligned film of liquid crystalline side-chain polymer and its subsequent thermal cycling through the biphasic region.

(Keywords: liquid crystalline; template; biphasic)

INTRODUCTION

Liquid crystalline side-chain polymers hold considerable promise as novel materials for advanced technology[1], and in particular as durable, low-fatigue media for optical information storage[2,3]. This technological potential stems from the hybrid character of the polymeric mesogens, which combine the electro-optic responses of low molar mass liquid crystals with the mechanical properties of polymers[4]. In addition to this highly desirable combination of properties, liquid crystalline side-chain polymers also exhibit some of the less desirable features of conventional polymers. Foremost amongst these is the difficulty in achieving reproducible synthesis[5], and the virtual impossibility in most systems of achieving the extremely high degree of purity that industry expects of low molar mass liquid crystals. In view of the fact that most polymeric mesogens will contain impurities, either in the form of low molar mass contaminants or in the form of a molecular weight distribution, it is desirable to obtain an understanding of how such impurities will affect the physical properties of the polymers. In a recent paper[6] Attard *et al.* made use of dielectric relaxation spectroscopy to observe the plasticizing effect resulting from the contamination of a siloxane side-chain polymer by the alkenic side-chain precursor, which appears to be a common impurity present in siloxane polymers[5].

In addition to plasticizing (or perhaps anti-plasticizing) effects, one of the important consequences of the presence of impurities in a mesogenic system is the tendency to promote phase separation in the neighbourhood of the mesophase–isotropic transition[7,8]. In the preceding paper[9], Attard *et al.* report an unusual phenomenon, associated with the phase separated region, which promotes the formation of macroscopically aligned mesophase. By using dielectric relaxation spectroscopy to probe the state of macroscopic alignment of a nematogenic siloxane polymer they found that the isotropic component of a biphasic system whose nematic component is homeotropic will, on cooling in the absence of external fields or surface forces, form a nematic phase which exhibits some degree of homeotropic alignment. The extent to which the newly formed phase attained homeotropic alignment was found to depend on the temperature in the biphasic through which the sample was cycled, and the number of such thermal cycles to which the sample was subjected[9].

In this paper we seek to define a simple phenomenological model based on the concept of template-induced alignment recovery to account for the observations of Attard *et al.*[9]. The model is expected to provide a theoretical framework on which an understanding of the processes that influence alignment in the mesophases formed by the complex side-chain polymers could be based.

A PHENOMENOLOGICAL MODEL OF TEMPLATE-INDUCED ALIGNMENT RECOVERY

To quantify the extent of macroscopic alignment it will be found convenient to introduce the quantity S_d (such that $-0.5 \leqslant S_d \leqslant 1.0$) which is formally defined as

$$S_d = \int_0^{\pi} P_2(\cos\beta) f_d(\beta) \sin\beta \, d\beta \qquad (1)$$

in which β is the angle between the local director and the laboratory *z*-axis, $P_2(\cos\beta)$ is the second rank Legendre polynomial, and $f_d(\beta)$ is the uniaxial orientational singlet probability distribution function of the local director. Apart from its conceptual simplicity, the advantage of using S_d to quantify the degree of alignment is that it is, in principle, accessible to experimental verification. For example, a reasonable estimate of S_d can be obtained from dielectric relaxation spectra as described previously[10,11].

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The general model

Consider a uniformly homeotropic nematic material at a temperature T_0 (such that $T_0 < T_\mathrm{N}$, the lowermost temperature of the coexistence region). On heating to T_i ($T_\mathrm{N} < T_\mathrm{i} < T_\mathrm{I}$) the material becomes biphasic and consists of a nematic component and an isotropic component in thermodynamic equilibrium. The respective volume fractions of the coexisting nematic and isotropic phases at T_i will be denoted by $\mathscr{V}_\mathrm{i}$ and $(1-\mathscr{V}_\mathrm{i})$. It is assumed that the various processes that lead to the randomization of the homeotropic alignment occur on an infinitely long time scale in comparison with the time scale of the experiments. Under such conditions, director alignment can only be destroyed by heating the material to a temperature $T_\mathrm{e} > T_\mathrm{I}$. Experimental observations[6,11,12] suggest that this is a reasonable assumption for the siloxane polymers studied. The overall degree of macroscopic alignment present in the biphasic material at T_i is therefore

$$[S_\mathrm{d}^{\{0\}}]_\mathrm{i} = \mathscr{V}_\mathrm{i} S_\mathrm{d} \tag{2}$$

where $S_\mathrm{d} = 1$ since the nematic component is uniformly homeotropic. The superscript $\{0\}$ denotes that the biphasic material has been formed by heating the initial homeotropic sample.

On cooling the material slowly to T_0, the $(1-\mathscr{V}_\mathrm{i})$ of isotropic phase is progressively converted into nematic phase. Our studies show that under these conditions the newly formed nematic phase will have acquired some degree of macroscopic alignment. The progressive change $(1-\mathscr{V}_\mathrm{i}) \to 0$ as $T \to T_\mathrm{N}$ means that the degree of alignment recovery is some complicated function of T_i. To obtain a simple and useful model it is assumed that on cooling from T_i to T_0 all of the $(1-\mathscr{V}_\mathrm{i})$ component forms a nematic phase having a uniform director alignment. After this first thermal cycle the sample is represented by a fully homeotropic component $\mathscr{V}_\mathrm{i}$ and a partially homeotropic component $(1-\mathscr{V}_\mathrm{i})$.

The extent to which the newly formed nematic phase recovers the initial homeotropic alignment is parametrized by $\lambda^{\{1\}}$ (such that $0 \leqslant \lambda^{\{1\}} \leqslant 1$). Accordingly, the overall alignment of the sample at T_0 after the first thermal cycle through the biphasic is

$$[S_\mathrm{d}^{\{1\}}]_0 = \mathscr{V}_\mathrm{i} + (1-\mathscr{V}_\mathrm{i})\lambda^{\{1\}} \tag{3}$$

In the limit where the isotropic component gives rise to fully homeotropic nematic $\lambda^{\{1\}} = 1$, while in the limit where the isotropic component forms a non-aligned mesophase $\lambda^{\{1\}} = 0$.

The next thermal cycle will involve the partial melting of the composite material formed in the first cycle. Clearly on heating to T_i the composite nematic phase will form a biphasic system consisting of $\mathscr{V}_\mathrm{i}$ composite nematic component and $(1-\mathscr{V}_\mathrm{i})$ isotropic component. Within the constraints imposed by this volume fraction conservation requirement, the nematic component may be of arbitrary composition. To aid the visualization of the melting process the sample is subdivided into an arbitrary number of cells as illustrated in *Figure 1*. The degree of macroscopic alignment within each cell is assumed to be uniform. This is colour-coded in *Figure 1* by using a grey scale in which white corresponds to fully homeotropic, black to random or isotropic and grey is intermediate alignment. As illustrated, after the first thermal cycle the nematic phase consists of a component that is fully homeotropic (white) and a partially aligned component (grey). On heating this composite material to T_i each component has a finite probability of melting subject to the volume fraction conservation condition.

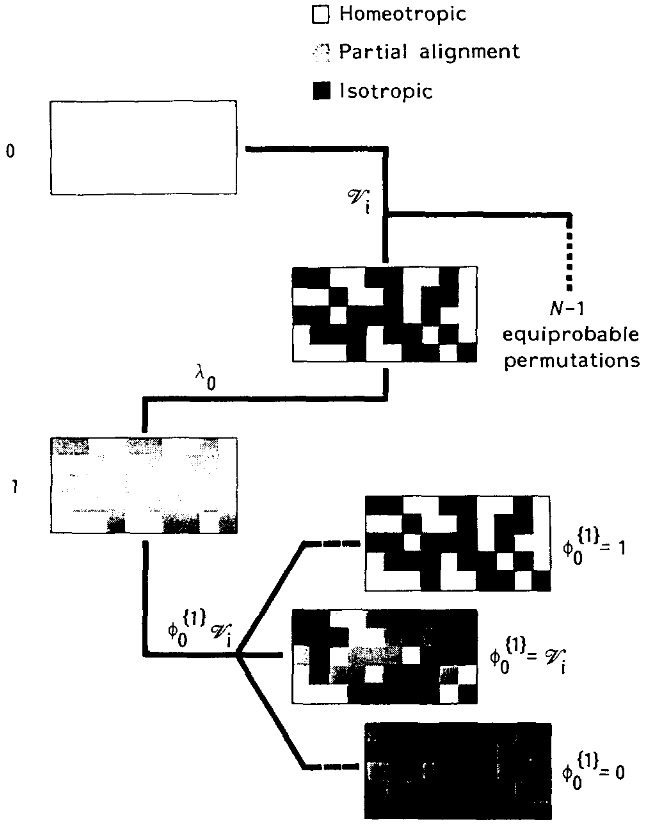

Figure 1 Schematic representation of alignment recovery and the subsequent melting process

From a purely combinatoric point of view the most likely outcome of the melting process is that $\phi_0^{\{1\}}$ of the homeotropic component and $\phi_1^{\{1\}}$ of the partially aligned component will persist in the biphasic such that $\phi_1^{\{1\}} = (1-\phi_1^{\{1\}})$ and $\phi_0^{\{1\}} = \mathscr{V}_\mathrm{i}$. This is equivalent to assuming that the homeotropic and partially aligned components will melt in the ratio of $(1-\mathscr{V}_\mathrm{i})/\mathscr{V}_\mathrm{i}$. The statistically least likely outcomes of the melting process involving the stylized material are those in which the material that melts to form the isotropic component in the biphasic tends to be derived from one or other of the two composite elements of the nematic phase. This corresponds to the cases when $\phi_0^{\{1\}} = 1$ or $\phi_0^{\{1\}} = 0$.

This approach may be extended to a material that has been thermally cycled through the biphasic regime. At T_0 the material is modelled as a composite system consisting of $(j+1)$ elements, each having its own value of S_d. Each time the sample is heated to T_i each element of the composite has a finite probability of melting and this probability of melting is reflected by the volume fraction of the element that actually melts, which is denoted by $(1-\phi_j)$ for the composite nematic material formed in the jth cooling cycle. The surviving volume fraction of this element will clearly still have a finite probability of melting during subsequent thermal cycles and in general this does not have to be related to any previous assignments of probability. In the $(k+1)$th cycle the volume fraction of the element that melts is given by

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$1-\phi_j^{\{k+1\}}$. By using this formalism it is trivial to show that the general model for template-mediated alignment recovery is given by

$$[S_{\mathrm{d}}^{\{n\}}]_0=\mathscr{V}_{\mathrm{i}}\left\{\prod_{q=1}^{n-1}\phi_0^{\{q\}}+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\left[\prod_{k=1}^{n-j}\phi_j^{\{k\}}\right]\right\}+(1-\mathscr{V}_{\mathrm{i}})\lambda^{\{n\}} \tag{4}$$

This equation contains too many independent variable parameters to be of use other than as a formal statement of the model. To obtain a description that is more easily related to experimental data the number of independent parameters must be reduced.

The simplified model

As was noted earlier, the relative volume fractions of nematic and isotropic components at T_{i} are independent of the number of thermal cycles. This conservation law can be stated formally as

$$\mathscr{V}_{\mathrm{i}}\left[\prod_{q=1}^{k-1}\phi_0^{\{q\}}\right]+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\left[\prod_{k=1}^{n-j}\phi_j^{\{k\}}\right]=\mathscr{V}_{\mathrm{i}} \tag{5}$$

It is next assumed that the generalized volume fractions $\phi_j^{\{k\}}$ are independent of k such that

$$\phi_j^{\{k\}}=\phi_j^{\{1\}}\ \forall k \tag{6}$$

and as a consequence of equation (5) it is found that

$$\phi_n=[\mathscr{V}_{\mathrm{i}}/(1-\mathscr{V}_{\mathrm{i}})](1-\phi_0^n)-\sum_{j=1}^{k-1}\phi_j^{n+1-j} \tag{7}$$

i.e. all the ϕ_j are determined by ϕ_0. (Note that the superscript $\{1\}$ has been omitted for convenience.)

It is appropriate at this stage to determine the physical significance of the assumption represented by equation (6). Described in the terms used previously to introduce the $\phi_j^{\{k\}}$, equation (6) states that the element that is formed during the jth cooling cycle will have the same probability of melting in subsequent heating cycles irrespective of the number of such cycles.

Given these simplifications, the expression for the average order of a sample after n thermal cycles is

$$[S_{\mathrm{d}}^{\{n\}}]_0=\mathscr{V}_{\mathrm{i}}\phi_0^{n-1}+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\phi_j^{n-j}+(1-\mathscr{V}_{\mathrm{i}})\lambda^{\{n\}} \tag{8}$$

in which the ϕ_j are related to ϕ_0 by equation (7). A further reduction in the number of independent parameters can be achieved by postulating a recurrence relation for the $\lambda^{\{j\}}$. The simplest model that can be employed in this context is one in which the extent of recovery is directly proportional to the overall degree of order present in the nematic component of the phase-separated system and to its volume fraction. Accordingly

$$\lambda^{\{n\}}=\lambda_0\left[\mathscr{V}_{\mathrm{i}}\phi_0^{n-1}+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\phi_j^{n-j}\right] \tag{9}$$

where λ_0 is the proportionality constant $(0\leqslant\lambda_0\leqslant 1/\mathscr{V}_{\mathrm{i}})$ such that when $\{n\}=1$

$$\lambda^{\{1\}}=\lambda_0\mathscr{V}_{\mathrm{i}} \tag{10}$$

Although more complicated recurrence relationships could be postulated, equation (9) would appear to mimic the experimental observations and so will be used to obtain the final statement of the simplified model:

$$[S_{\mathrm{d}}^{\{n\}}]_0=[1+\lambda_0(1-\mathscr{V}_{\mathrm{i}})]\left[\phi_0^{n-1}\mathscr{V}_{\mathrm{i}}+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\phi_j^{n-j}\right] \tag{11}$$

which is an expression in terms of three independent parameters, namely, λ_0, $\mathscr{V}_{\mathrm{i}}$ and ϕ_0. It is instructive to determine the behaviour of this simple empirical model for extreme values of these three parameters.

In the limit where the volume fraction of the nematic component vanishes, equation (11) reduces to

$$S_{\mathrm{d}}^{\{n\}}|_{\mathscr{V}_{\mathrm{i}}\to 0}=(1+\lambda_0)\sum_{j=1}^{n-1}\lambda^{\{j\}}\phi_j^{n-j} \tag{12}$$

However it can be seen from equation (7) that the ϕ_j vanish for all j when $\mathscr{V}_{\mathrm{i}}=0$ and therefore

$$S_{\mathrm{d}}^{\{n\}}|_{\mathscr{V}_{\mathrm{i}}\to 0}=0 \tag{13a}$$

Conversely as $\mathscr{V}_{\mathrm{i}}\to 1$

$$S_{\mathrm{d}}^{\{n\}}|_{\mathscr{V}_{\mathrm{i}}\to 1}=1 \tag{13b}$$

If no alignment recovery occurs during the first cooling cycle $\lambda_0=0$ and so

$$S_{\mathrm{d}}{}^{\{n\}}|_{\lambda_0\to 0}=\phi_0^{n-1}\mathscr{V}_{\mathrm{i}} \tag{14a}$$

Equation (14a) is an asymptotically decreasing function of n. As $\lambda_0\to 1/\mathscr{V}_{\mathrm{i}}$ (complete recovery)

$$S_{\mathrm{d}}{}^{n}|_{\lambda_0\to 1/\mathscr{V}_{\mathrm{i}}}=1 \tag{14b}$$

Finally, the effect of ϕ_0 on $S_{\mathrm{d}}^{\{n\}}$ can be seen from the limiting values $\phi_0=0$, $\mathscr{V}_{\mathrm{i}}$, 1

$$S_{\mathrm{d}}^{\{n\}}|_{\phi_0\to 0}=[1+\lambda_0(1-\mathscr{V}_{\mathrm{i}})]\left[(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\phi_j^{n-j}\right] \tag{15a}$$

where ϕ is a function of $\mathscr{V}_{\mathrm{i}}/(1-\mathscr{V}_{\mathrm{i}})$ only,

$$S_{\mathrm{d}}^{\{n\}}|_{\phi_0\to\mathscr{V}_{\mathrm{i}}}=[1+\lambda_0(1-\mathscr{V}_{\mathrm{i}})]\left[\mathscr{V}_{\mathrm{i}}^n+(1-\mathscr{V}_{\mathrm{i}})\sum_{j=1}^{n-1}\lambda^{\{j\}}\mathscr{V}_{\mathrm{i}}^{n-j}\right] \tag{15b}$$

$$S_{\mathrm{d}}^{\{n\}}|_{\phi_0\to 1}=[1+\lambda_0(1-\mathscr{V}_{\mathrm{i}})] \tag{15c}$$

RELATION BETWEEN MODEL AND EXPERIMENT

Although equation (11) has three independent parameters it is possible to obtain estimates for λ_0 and $\mathscr{V}_{\mathrm{i}}$ from dielectric data. If the biphasic material formed in the first heating cycle is shock-cooled to T_0 it is found that no alignment recovery occurs[12] and accordingly following the arguments outlined previously we deduce that

$$S_d^{\{1\}}|_{\text{shock-cooled}} = \mathscr{V}_i \qquad (16)$$

The values of $S_d^{\{1\}}|_{\text{shock-cooled}}$ determined from the dielectric loss data are listed in *Table 1*, from which estimates of $\mathscr{V}_i$ are obtained as shown in *Figure 2* (see ref. 9).

From equation (11) it follows that

$$S_d^{\{1\}} = 1 + \lambda_0(1 - \mathscr{V}_i) \qquad (17)$$

and since $\mathscr{V}_i$ is known, $S_d^{\{1\}}$ is obtained from experiment (*Table 1*), λ_0 can be estimated. This leaves only ϕ_0 as a variable parameter with which to fit the experimental data and the results of such a fit are shown in *Figure 3*, from which it can be seen that the simple theory provides an excellent model for the experimental observations.

DISCUSSION

The most striking feature to emerge from the fits is that $\phi_0 \neq V_i$ except when $\mathscr{V}_i \rightarrow 1$. This feature is shown quite clearly by *Figure 4* in which ϕ_0 is plotted against $\mathscr{V}_i$. For purely statistical melting the combinatoric approach described earlier would predict that $\phi_0 = \mathscr{V}_i$ and this should result in a straight line as indicated in *Figure 4*. The fitted values for ϕ_0 are always greater than $\mathscr{V}_i$. It will be recalled that the physical significance of $\phi_0 = 1$ is that the same portion of material tends to melt during each thermal cycle. Clearly by relating the model to the data it is found that the material exhibits some tendency for the same portions to melt, leading to a less drastic degree of alignment loss than would otherwise occur. This observation is also confirmed by optical microscopy on the sample investigated.

It is well known that for low molar mass mesogens the presence of a coexistence region results in an unequal partitioning of chemical species between the two component phases[7], with the isotropic component becoming progressively richer in the lower molar mass species. Our observations indicate that the time scale for the diffusion of these low molar mass species through the sample at T_0 is long in comparison with the time scale of the experiments. The slow diffusion results in the formation of regions that have a high concentration of low molar mass components. Clearly these regions will always melt preferentially to the regions containing the higher molar mass components.

Table 1 Values of director order parameter for sample obtained by shock-cooling the biphasic material (for further details see text)

T (K)	$S_d^{\{1\}}\|_{\text{shock cooled}}$
314.9	0.99±0.01
315.4	0.89±0.02
315.9	0.77±0.02

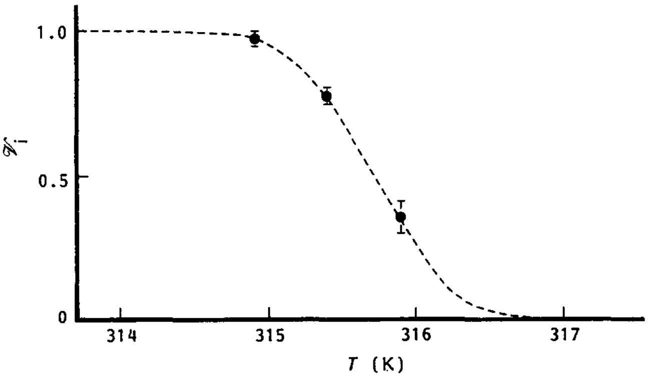

Figure 2 Volume fraction of the nematic component of the biphasic material as a function of temperature. The volume fraction has been estimated from the shock-cooled material as described in the text and in Reference 11

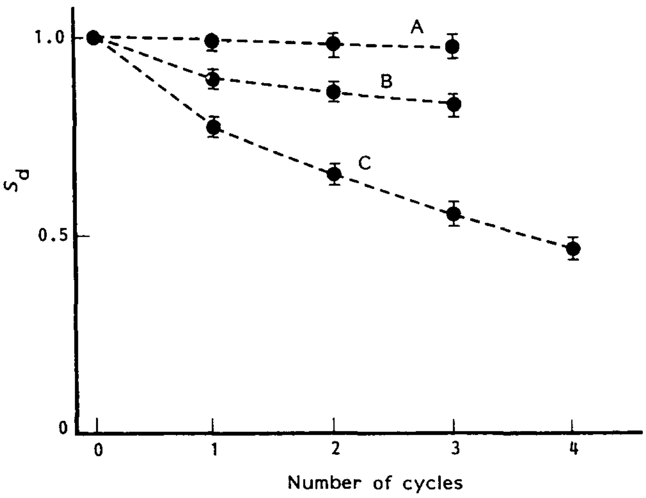

Figure 3 Theoretically predicted values of $S_d(0)$ as a function of the number of thermal cycles through the biphasic region. Cycling temperatures: A, 314.9 K; B, 315.4 K; C, 315.9 K. Experimental points are shown as ●

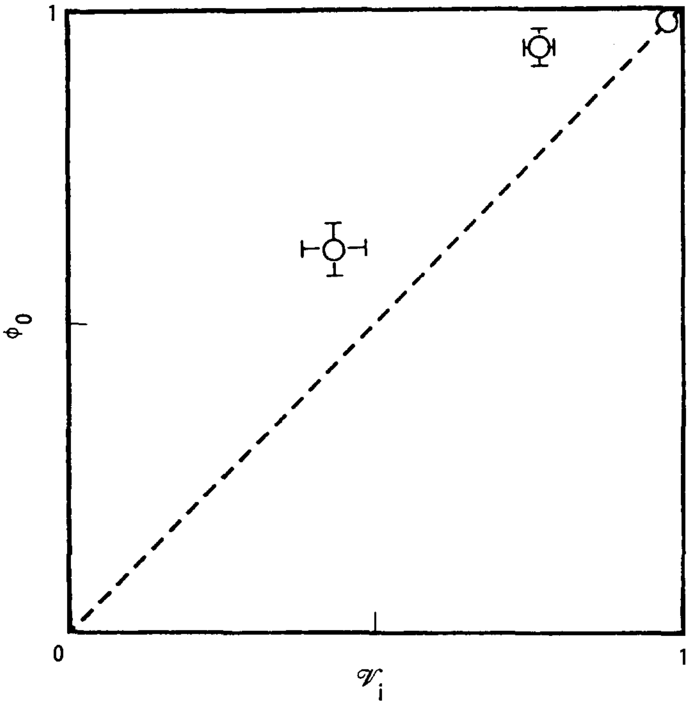

Figure 4 Plot of ϕ_0 against fraction of nematic component

These observations have important implications for the use of liquid crystalline side-chain polymers as solutes in guest–host systems intended for field-assisted thermal erase/write (FATE/W) applications since they pinpoint a possible source of device irreproducibility.

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