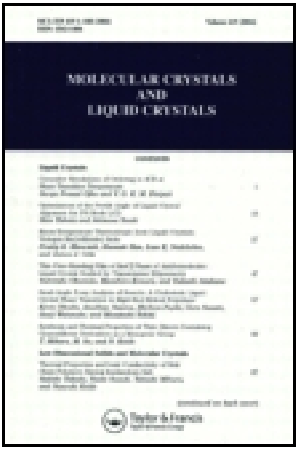

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Microstructure of Side Chain Liquid Crystalline Polymers and their Alignment Using Electric Fields and Surfaces

R. B. Findlay [a]

[a] Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

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Microstructure of Side Chain Liquid Crystalline Polymers and their Alignment Using Electric Fields and Surfaces

R. B. FINDLAY
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

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The current understanding of the ordering and dynamics of backbones, flexible spacers and side groups in side chain liquid crystalline polymers (SCLCPS) is reviewed. Comparisons are made between theoretical work and the experimental results from small angle neutron scattering (SANS) and dielectric relaxation spectroscopy (DRS). Alignment of SCLCPS by AC and DC electric fields, as studied using DRS, optical microscopy, and transmitted light techniques are also reviewed, and the less well understood field of surface alignment is mentioned.

Keywords: side chain, liquid crystal, polymer, alignment, electric, surface

BACKBONE ORIENTATION AND SIDE GROUP DYNAMICS

SCLCPS combine the mechanical properties of conventional polymers with the useful device properties of small molecule liquid crystals (SMLCS); examples of SCLCP alignment are illustrated by Attard and Williams[1] in Figure 1. The SCLCP may not form a liquid crystalline phase if the backbone interferes too much with its movements, it must be decoupled using a flexible spacer, so there are three important parts of the structure: the backbone, the flexible spacer, and the mesogenic group itself.

Backbone Trajectory

The more flexible the backbone, the less the influence it has on the side groups, and (in nematics) the lower T_{NI}. For instance, a siloxane backbone is quite flexible, whereas a methacrylate backbone is more rigid. The flexibility of a system with strongly ordering side groups can be increased by copolymerising with monomer units which are not substituted with side groups. This lowers the mesogen content and may improve the mechanical properties. Yamaguchi *et al.*[2] studied several such series of copolymers, and found that, as the mesogenic content fell, the mesophase-isotropic transition temperature (clearing point) fell also. The rate at which the

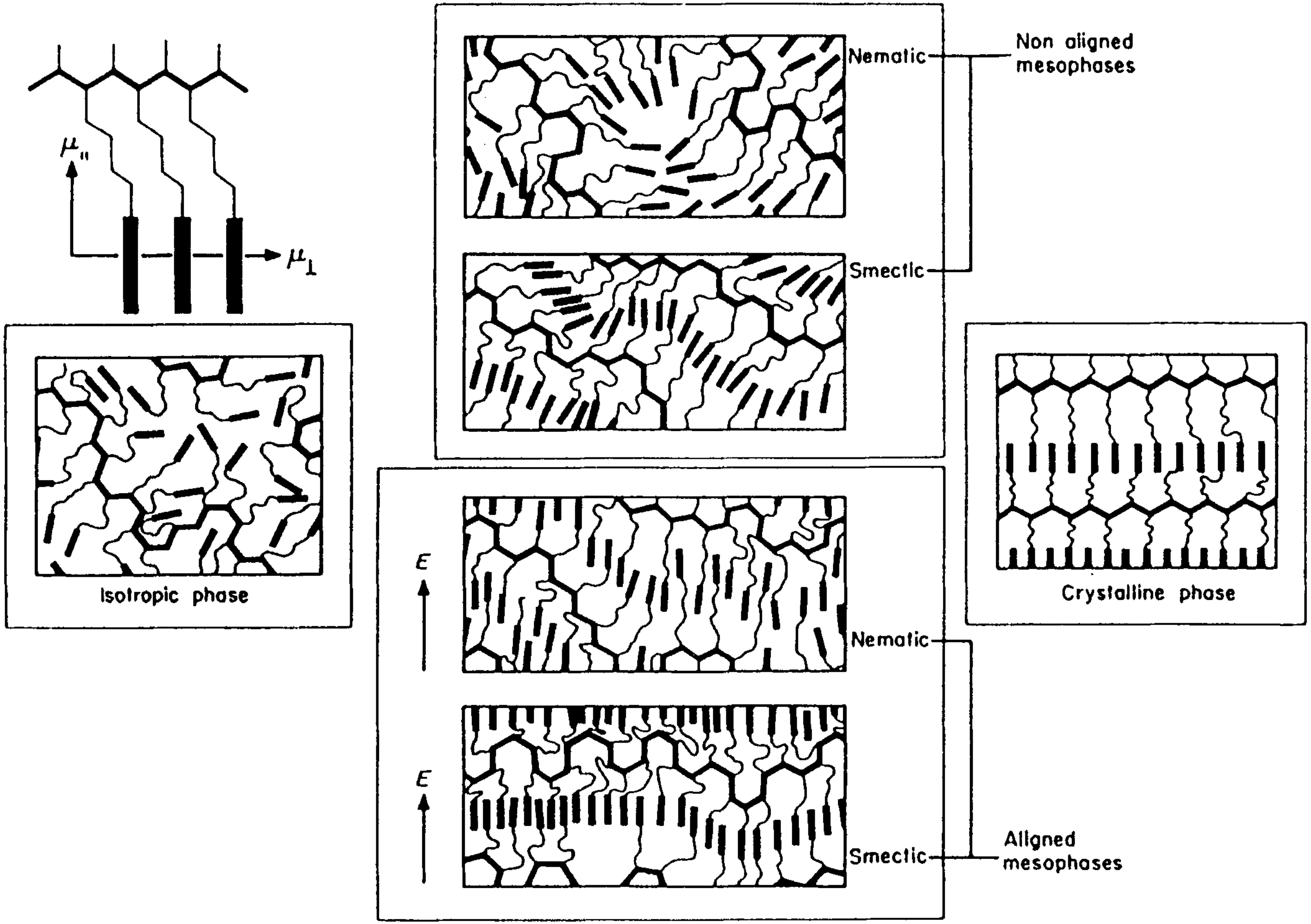

FIGURE 1 Backbone and side group structure for different phases of a SCLCP (from G. S. Attard and G. Williams, *Polym. Commun.* **27**, 2–5 (1986) by permission of the publishers, Butterworth Heinemann Ltd.).

clearing point fell was greater if long or bulky chains were attached to the unsubstituted backbone units. Liquid crystalline properties may be lost altogether if substitution with non-mesogenic groups lowers the clearing point below the glass transition temperature, as seen by Findlay *et al.*[3,4]

There are different types of backbone/side-chain ordering in SCLCPS, and a review of the theoretical and experimental work was given by Noirez and Pépy in 1989.[5] According to Wang and Warner[6] and Warner[7] there are three types of order in a nematic (Figure 2), and he presents a phase diagram based on the volume fraction of side groups. If the side groups dominate the ordering, the backbone is limited mainly to directions normal to the director (nematic phase N_I), which is the most common type. If the backbone dominates and wants to align parallel to other backbone segments, then the side groups have to align normal to it (nematic phase N_{II}). Finally, if the backbone and side chains want to lie parallel to each other, we have nematic phase N_{III}.

Renz and Warner[8] predict that backbones in smectics A are not only under similar directional constraints to the nematic N_I phase, but are also confined to the planes between the layers of side grops. If the backbone hops from one layer to the next there is an energy penalty, because the side groups which are attached to the hopping backbone segment are in conflict with the ordering field (Figure 3). This energy penalty encourages the hopping segment to be as short as possible, which means that it must lie nearly parallel to the layer normal. The radius of gyration of the backbone $R_\parallel$ parallel to the layer normal follows an activation law, varying according to

$$R_\parallel^2 \propto e^{-E/kT}$$

where E is the energy penalty, k is the Boltzmann constant and T is the temperature.

Rieger[9] also considers the volume occupied by the backbone by modelling the trajectory as any of four kinds of two-dimensional random walk between the smectic layers: pure random walk (Figure 4), self-avoiding walk, compact self-avoiding walk, and straight walk (Figure 5). Of these, the straight walk (where the backbone

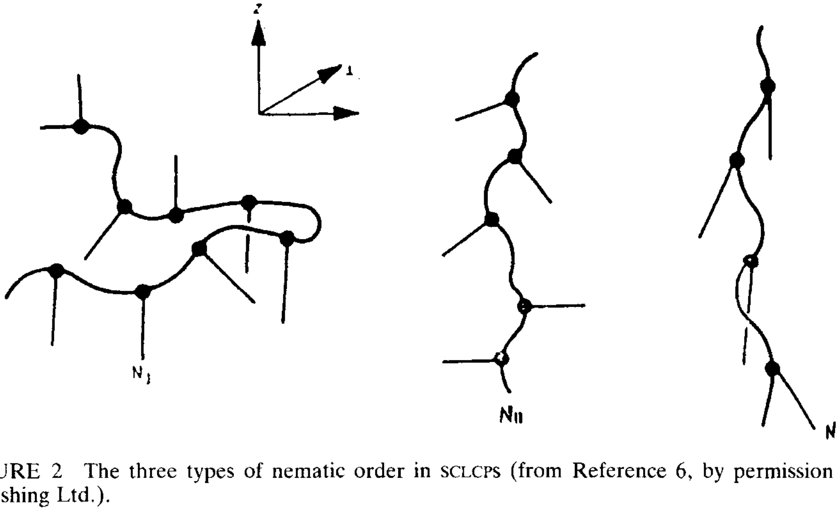

FIGURE 2 The three types of nematic order in SCLCPS (from Reference 6, by permission of IOP Publishing Ltd.).

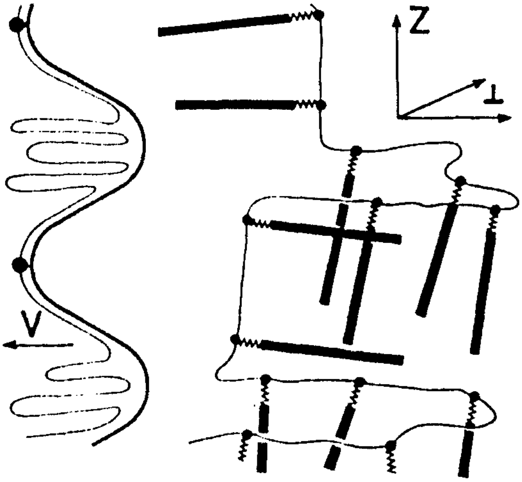

FIGURE 3 Origin of the energy penalty for layer hopping by the backbone in a sinusoidal potential shown (from Reference 8).

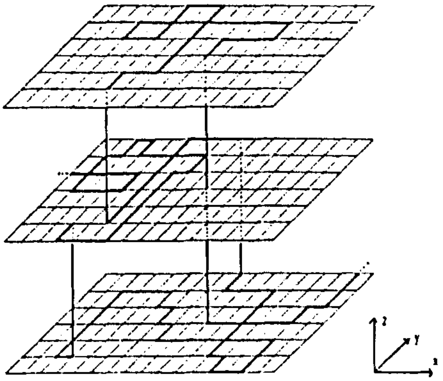

FIGURE 4 Pure random walk of the backbone in a smectic A SCLCP (from Reference 9).

moves along only one randomly chosen direction in each layer), with entanglements (Figure 6), is said to fit the experimental data most closely. Also, Kunchenko and Svetogorsky[10] have related the number of layer-hopping backbone segments to $R_{\|}$.

Small angle neutron scattering (SANS) is the most important technique for determining the backbone trajectory. Backbones were shown to be confined between the side chain layers in all the smectic SCLCP samples studied.[5] Keller *et al.*[11] and Hardouin *et al.*[12] studied SCLCPs with deuterated methacrylate backbones, one with a —OC_4H_9 terminator, the other with a —CN terminator. The results are shown in Figure 7. The smectics both show strong confinement of the backbone into planes, following the activation law with $E = 0.8$ eV.

They also observed small angle diffuse spots which correspond to a spacing of 56 Å, which is almost twice the smectic layer spacing of 29.5 Å, and which have a weak periodicity of 38 Å perpendicular to the magnetic field. This leads them tentatively to suggest the microstructural model shown in Figure 8.

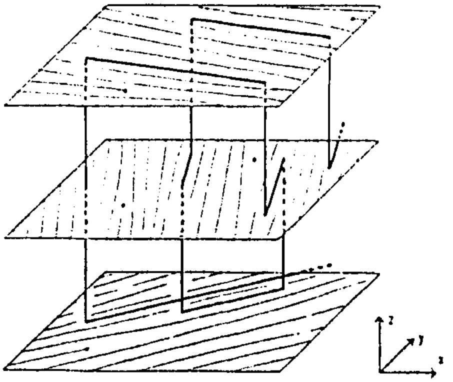

FIGURE 5 Straight walk of the backbone in a smectic A SCLCP (from Reference 9).

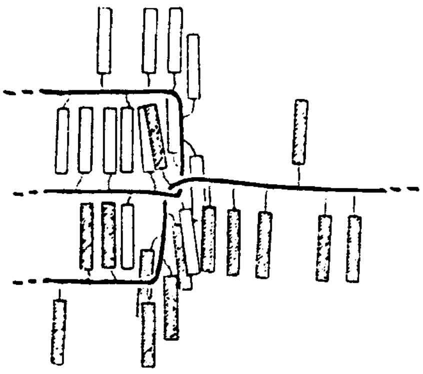

FIGURE 6 An entanglement in a smectic A SCLCP (from Reference 9).

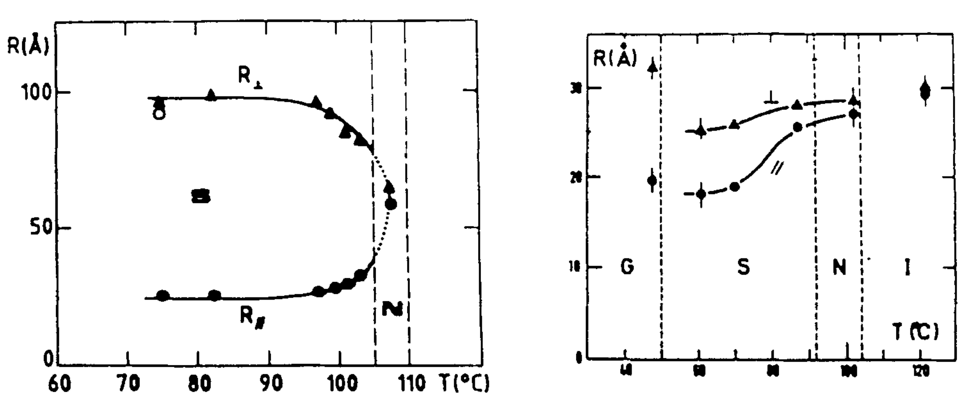

FIGURE 7 Radius of gyration of polymethacrylates, illustrating backbone confinement (from Reference 5). Left: —OC_4H_9, right: —CN terminated.

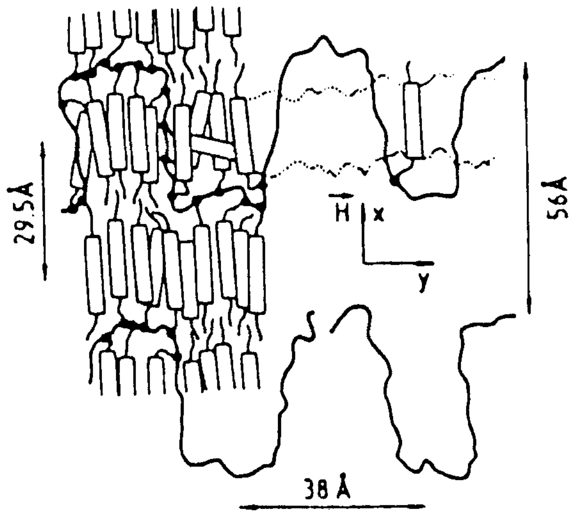

FIGURE 8 A proposed model for a smectic A, showing some bilayer structure (from Reference 5).

SANS studies of polysiloxanes use polymers with deuterated spacers or side groups, so the backbone trajectory is not measured directly. Hardouin *et al.*[12] and Kalus *et al.*[13] show that polysiloxane backbones also show an oblate anisotropy, and the backbones are thought to be trapped into planes between the smectic side group layers with occasional layer hopping. The nature of the anisotropy in nematics was ambiguous, due to problems with the position of the deuteration, but it is likely that the nematics also show some degree of oblate anisotropy.

The high flexibility of a siloxane backbone is illustrated by the following example from Diele *et al.*[14] They diluted a smectic side chain polymer (with a siloxane backbone) by inserting dimethylsiloxane units into the backbone (i.e. which did not have side groups attached). They found that the smectic layer spacing increased approximately linearly with the number of dimethylsiloxane units per side chain, showing that the backbone was coiling up between the smectic layers so that the side goups could maintain a constant interchain packing density. This is an unusually dramatic example (confirmed by Richard *et al.*[15]) of the backbone trajectory being controlled by phase segregation in side chain materials. A significant degree of disordering would be expected instead in the layers of SCLCPs with stiff methacrylate backbones.[3]

Side Group Motions

The backbone and side groups are mobile within the smectic structure, and different kinds of motion become active above different temperatures. These are studied using dielectric relaxation spectroscopy (DRS). In DRS, two quantities are measured: the permittivity and the dielectric loss. A full treatment of DRS theory, such as that by Kozak *et al.*[16] is beyond the scope of this review, and descriptions of the principles are found in standard texts.[17]

Zentel, Strobl and Ringsdorf[18] studied polyacrylates and polymethacrylates with mesogenic side groups, and have identified and named the relaxation processes illustrated in Figure 9. They say:

> 'The relation between the α- and δ-relaxation and the state of order of the system is different for the polyacrylates and the polymethacrylates. In case of the polyacrylates the δ-relaxation peak passes continuously without abrupt intensity changes through all mesophases and the isotropic phase. The phase transitions leave the state of this motion unchanged. This is in agreement with similar observations on low molecular weight liquid crystals. The polymethacrylates show a qualitatively different behaviour. For [one sample] the δ-motion is setting in at about 107°C together with a [smectic A-nematic] phase transition. The observation indicates that this phase transition differs in character from the usual smectic-nematic transition and incorporates as an additional factor an abrupt change in the state of motion.'

Attard *et al.*[19] and Haase and Pranoto[20] note the large decreases in frequency for the α process, and the smaller decrease in the δ process rate, on moving from a SMLC to a siloxane or acrylate nematic SCLCP system. Attard *et al.*[19] consider that the α process is not due to cooperative motions via the backbone, but that the δ process is. They also cast doubt on the assertion that the δ process is a flip-flop motion of the long axis of the side group, bearing in mind the constraints imposed on the system by the presence of the backbone, and suggest a conical motion of the side groups instead.

However, Pranoto *et al.*[21] have no doubts in saying that the δ process is due to 'reorientations of the mesogenic unit around the main chain,' and that their results 'clearly demonstrate that this process only contributes to $\varepsilon_{\parallel}$.' On the effect of the length of the flexible spacer in a copolymer incorporating two different spacer lengths:

> '. . . we have a copolymer with different mesogenic units and spacer lengths. If the parallel process were caused by independent motions of the monomeric unit, one should expect to find two separate relaxation frequencies of the two monomeric units. Kresse *et al.*[22] for example, have shown that the spacer length strongly influences the relaxation frequencies of liquid crystalline side chain polymers. The absence of separation suggests that on the contrary this process is better described by collective motions of the mesogenic side chains.'

This relaxation frequency jumps at the clearing point, when the loss of the nematic field reduces the activation energy for the side group motion. As expected,

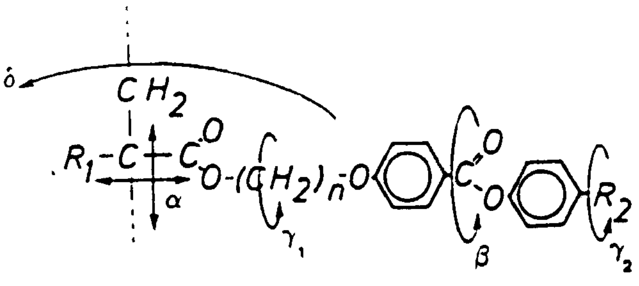

FIGURE 9 Dielectrically observed relaxation processes (Reprinted with permission from R. Zentel, G. R. Strobl and H. Ringsdorf, *Macromol.*, **18**, 960–965 (1985). Copyright (1985) American Chemical Society).

a longer flexible spacer results in a higher relaxation frequency due to better decoupling.

Kresse and Talrose[23] and Haase *et al.*[24] studied relaxation processes in nematic SCLCPs with acrylate backbones. They also assign the δ process, which is prominent in the $\varepsilon_{\parallel}$ relaxation, to the motion of side groups around the backbone, because it is the strongest relaxation (and is therefore due to the strongest dipole, which is on the mesogenic group) and it is also found in SMLC equivalents. The $\varepsilon_{\perp}$ relaxation is due to several processes in the main and side chains. There is a small active process in the glassy phase, where motion might not be expected, but this is merely due to the rotation of an ester link in the mesogenic group.

Bormuth and Haase[25] found that the activation energy for the side group reorientation varied according to the type of backbone, increasing along the series acrylate-methacrylate-chloroacrylate. The δ process frequency in SCLCPs with acrylate and methacrylate backbones is sensitive to the conformation of the backbone, which can change according to the crystalline state.

A survey of different smectic and nematic SCLCP homo- and co-polymers with siloxane backbones was conducted by Haws *et al.*,[26] who found that the greater free volume in the copolymers allowed freer movement of the side groups, resulting in lower activation energies and improved peak resolution. Kresse *et al.*[27] found that the relaxation frequency was about a thousand times slower in their smectic than in their nematic polymer. The smectic-isotropic transition was also marked by a much larger step in the relaxation frequency than the nematic-isotropic transition, which they attribute to the greater ordering in the smectic phase.

The problem of resolving peaks in homopolymers has been tackled by Attard[28] who fitted two curves to broad, asymmetrical experimental results to simulate the addition of two processes. He found that for the molecule chosen (an unaligned nematic polysiloxane) the δ peak was smaller than the α peak in all phases, completely contrary to what would be expected by looking at the unprocessed data. He confirmed that the δ peak was narrow and due to a single process, whereas the α peak was broader and may be due to more than one process.

ELECTRIC FIELD ALIGNMENT

Finkelmann, Naegele and Ringsdorf[29] were the first to report that SCLCPs show much the same properties as SMLCs but with slower response times. SCLCPs have the huge advantage that the aligned textures are not only frequently stable up to the clearing point (especially in smectics), but that the alignment can be frozen in below the glass transition temperature.[30] The emerging technologies for applying these materials to display and recording devices have been reviewed by Nakamura *et al.*[31] The alignment increases the order of the side groups, but the ordering in the flexible spacers decreases substantially, as evidenced by a sharp fall in the trans-gauche ratio.[32]

Polymers also display electrohydrodynamic instabilities, and the higher viscosity allows more detailed characterisation of the precursor textures.[33,34] These instabilities can result in partial alignment, as the shear forces produced have an aligning effect on the molecules. A comprehensive review and reclassification of instabilities in SMLCs was given in 1982 by Blinov *et al.*^{35} Figure 10 broadly summarises the instability domains, although not all materials follow the same pattern. There are two important modes of instability: anisotropic and isotropic. Anisotropic modes occur only in anisotropic liquids, such as liquid crystals. There are many types, which include Williams domains in low frequency fields (when the conductivity anisotropy is most important) and chevrons in high frequency fields (when the dielectric anisotropy is most important). Isotropic modes can occur in any liquids, including anisotropic ones. There are two main types: the Felici instability, which is stirring caused by charge injection, and a high frequency mode caused by non-uniform fields near the electrodes.

Poling requires the application of strong DC fields to the material, which is a good way to develop the Felici instability. This is why SCLCPs are good candidates for NLO materials, as they have a glass transition at which to pole the material, where the side groups can move with the field but the backbone is immobile enough to prevent instabilities from developing.

Talrose *et al.*^{36} found that the response time was faster at higher temperatures (in their nematic polymer), and found that the response time $\tau \propto V^{-2}$, which is the same as for nematic SMLCs. The slow response is a major obstacle to the use of SCLCPs in display devices. Ringsdorf and Zentel^{37} found that the response time at constant temperature is determined (in the nematic polyacrylic ester they studied) by the difference between the glass transition and ambient temperature. There is therefore an incentive to synthesise materials with $T_g < 0°\mathrm{C}$ for display applications at room temperature. The fastest response times have been of the order of a hundred milliseconds for active processes in thin samples and the response is usually very slow in both nematics and smectics except at temperatures very close to the clearing point or in the biphasic region.$^{30,32,34,38-43}$

For this reason, many workers align their samples while cooling them from the isotropic phase,^{30,34,41,42,43} and it is found that better alignment is obtained at slower

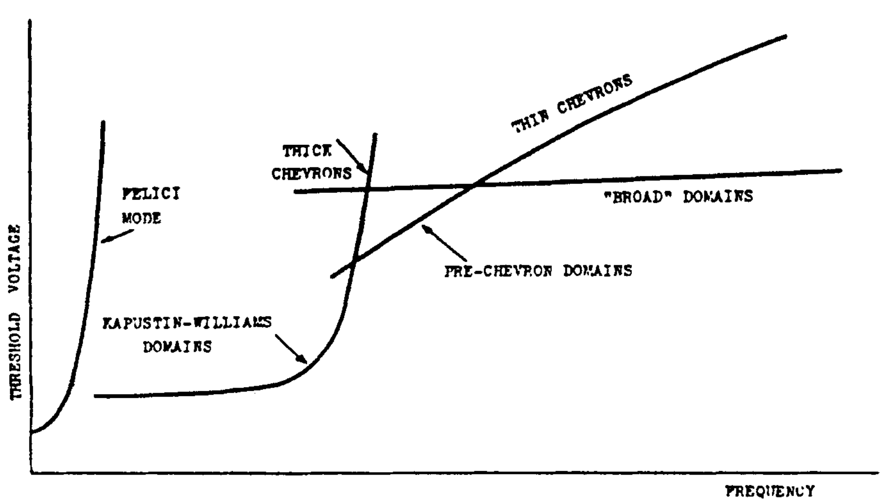

FIGURE 10 Electrohydrodynamic instability regimes (from Reference 35).

cooling rates.[30,41] The faster response at the clearing point is thought to be due to the drop in viscosity,[32,40] and smectics particularly show a steep increase in response time as the temperature is lowered.[43,44] Also, more flexible, lower viscosity backbones such as siloxanes and acrylates allow faster response times than methacrylate backbones,[20,32,43] as does a material whose viscosity has been lowered by impurities.[44] This is shown by the passive decay time for nematics, which varies according to η_1/k_{11}, where η_1 is a viscosity and k_{11} is an elastic constant.[45]

There is usually a threshold voltage V_c for alignment at constant temperature which is dependent on $(k_{11}/\Delta\varepsilon)^{1/2}$, where $\Delta\varepsilon$ is the dielectric anisotropy,[45] although sometimes a threshold effect is not seen.[1] Threshold effects are also seen for alignment during constant cooling.[30] Even if the response times are poor, long flexible spacers can lower k_{11}, and hence V_c, to around that of the corresponding monomer. This means that long spacers can achieve good decoupling from the backbone for static processes but not for dynamic ones,[37] and also have the benefit of raising the clearing point and lowering the glass transition.[40] A comparison of SMLC and SCLCP properties is given in Table I.[37]

Scattering textures can be deliberately produced by applying a DC electric field,[30,39,43] although it is well known that the charge injection processes can cause liquid crystals to decompose rapidly[37] so low frequency AC fields are usually preferred.[33,39,40] Findlay and Windle[3,34] observe an electrohydrodynamic instability in strong DC fields which is not due to an isotropic charge injection mode, but unfortunately limited charge injection does damage their material. As already mentioned, DC poling fields are usually applied at temperatures around the glass transition to avoid this sort of problem, but Kozak *et al.*[46] have successfully caused a significant degree of alignment in a chiral nematic SCLCP using DC fields 9°C below the clearing point. The maximum order parameter was only 0.25 (compared with 1.0 for a perfectly aligned homeotropic sample), and it is not clear whether this may be due in part to instabilities or to the known conductivity effects. Numerical modelling studies of this effect[47] suggest that the planar-homeotropic transition occurs first by bend, and then by splay, although the models presented predict far higher order parameters (close to 1) than found by experiment, and did not appear to allow for the presence of instabilities. Conductivity effects can be reduced by DC cleaning,[48] in which ions are swept out of the material to the electrodes by annealing in a DC field.

The effect of alignment on the dielectric relaxation has been extensively studied, mainly by Williams, Attard and co-workers,[1,16,41,42,44,46–55] and dielectric relaxation spectroscopy (DRS) can be used to measure the order parameter of an aligned material. As the homeotropic orientation increases (using stronger AC fields), the

TABLE I

Electrical Freedericksz transitions (from Reference 37)

Quantity	SMLC	SCLCP
Threshold voltage	5 – 10 V	8 – 80 V
Rise time	30 ms – 1 s	200 ms – 2 s
Decay time	30 ms – 1 s	200 ms – 10 s
Temperature range	−10°C – 70°C	80°C – 190°C
Sample thickness	10 μm	20 μm

δ process becomes stronger (by a factor of three[49]) and the α process almost disappears. Conversely, strong planar alignment causes the α process to become prominent, and the δ process to disappear (see Figure 11). The presence of a crossover frequency ν_c, which rises with increasing temperature, makes both kinds of alignment possible, and in one material studied (a nematic polysiloxane)[42] the dielectric anisotropy was positive (for homeotropic alignment) below ν_c and negative (for planar alignment) above it. The temperature dependence of ν_c means that materials which are aligned while continuously cooling them through the transition from the isotropic phase are usually aligned homeotropically.

The alignment at phase transitions can be monitored this way, and it is found that the δ peak varies continuously in height while alignment takes place through the biphasic region in a nematic polysiloxane.[56] The δ peak also moves to higher frequencies as the energy of the system increases at higher temperatures, as is common in solid polymers.[50]

Returning to the issue of relating relaxation peaks to molecular motions, the α and δ peaks have recently been related to four basic modes of relaxation by Attard,[28] and this theory is summarised by Kozak *et al.*[55]:

> 'Subscripts 00, 01, 10, and 11 denote the basic modes of relaxation; 00 mode is associated with the end-over-end reorientation of the mesogenic group, 01 with reorientation about its long axis, 10 with so-called stochastic precession and 11 is a combination of the precession and reorientation about the long axis . . . the theory is general and does not predict the particular shape of each peak (which, in turn, has to be related to the particular mechanisms of the stochastic motions involved) . . . the low frequency peak of the unaligned sample is associated with the 00 mode while the high frequency combines the 01, 10, and 11 modes . . . for aligned samples the theory directly links peaks for the homeotropic sample with the 00 and 01 modes while for the planar one are linked with the 01 and 11 modes.'

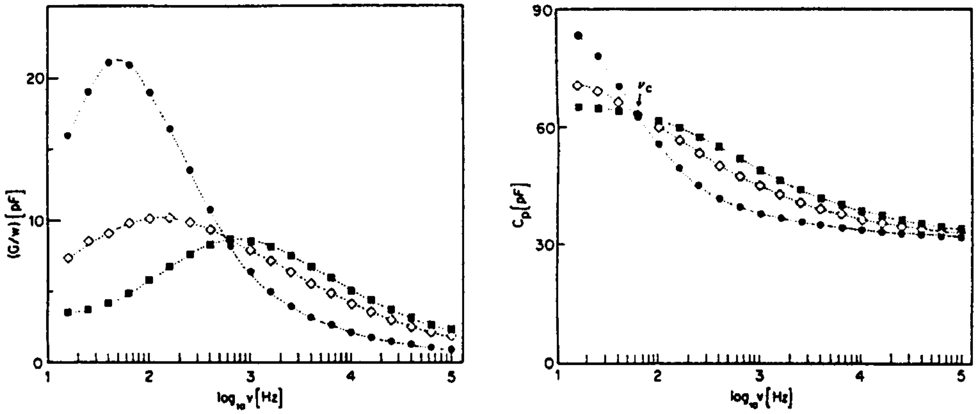

FIGURE 11 Frequency dependence of G/ω (proportional to the loss factor ε'') and C_p (linear in the dielectric permittivity ε') for a homeotropically aligned (filled circles), planarly aligned (filled squares) and unaligned (empty diamonds) nematic polysiloxane (from G. S. Attard, K. Araki and G. Williams, *J. Molec. Electr.*, **3**, 1–7 (1987)). Copyright (1987) by John Wiley & Sons, Ltd. Reprinted with permission.

Another probe which can be used to study alignment is transmitted light. The present review will not deal here with non-linear optical measurements, waveguiding, or the rotation of polarised light by twisted textures, but will concentrate on polarised light effects.

Much optical analysis work involves nothing more sophisticated than a photodiode stuck to the eyepiece of a microscope, while the sample undergoes field and/or heat treatments between crossed or parallel polars.[30,38–40,43,57–64] This method is commonly used merely to generate an electronic signal so that the rate of a given optical effect can be measured automatically, or to measure the temperature of a phase transition as an alternative or supplement to DSC.

There is an interesting variation on this technique in which the light is still transmitted normal to the sample, but the tilt of the director relative to the light is continuously variable, giving rise to interference fringes as the birefringence develops.[20,37,45,65,66] This method allows the alignment to be measured against voltage, time or temperature, so long as the sample is sufficiently transparent.

To study the development of homeotropic alignment, either the whole conoscopic image must be monitored, or the sample must be tilted off-axis and the polars set at 45° to the plane of tilt as in the technique of Findlay *et al.*[3,34] Their method was used to monitor the alignment in electric fields of a smectic A SCLCP, observing the extension of the biphasic region to lower temperatures than was detectable using DSC and distinguishing these effects from those due to backbone relaxation. Their technique effectively samples a part of the conoscopic image.

It is remarkable how few workers have used such optical techniques, particularly in the study of smectic alignment. One reason is that smectic textures commonly scatter light, which makes analysis of the results complicated. For all phases, most workers prefer to use more direct measurements such as those from NMR and DRS. A great advantage of optical methods is that they are relatively easy to use, and yield results quickly using simple apparatus, even though quantitative analysis of the results can be difficult. The recent availability of microscope objective lenses which allow the whole conoscopic image to be observed even at the long working distances involved with hostage work may prompt a revival in the use of transmitted polarised light techniques.

SURFACE ALIGNMENT

Surface alignment is critical to the twisted nematic display, as it provides the driving force for the voltage-off state. As a result, considerable research has focussed on the anchoring and alignment of nematic SMLCs by surfaces of various types.

Alignment by surfaces can be more difficult in SCLCPs than in SMLCs, but can still have a significant effect.[4,30,37] Surface alignment is important for experiments based on the electro-optic effects currently exploited in twisted nematic displays,[45] but is said not to be a prerequisite for good electro-optical properties in SCLCPs.[38,39,62,63]

It is sometimes remarked informally, however, that some degree of alignment *is* necessary for clear, aligned SCLCP textures. This is not often stated explicitly in the literature because most workers (who may have previously studied SMLCs, which require deliberate surface treatments for alignment) casually use sample preparation techniques which automatically cause some backbone alignment due to flow (such as allowing capillary action to draw the polymer into a sandwich cell). It may be that this simply reduces the density of entanglements in the polymer backbones, and therefore reduces the density of defects, but it is likely that this will also cause some planar anisotropy in the backbone.[34] This would aid the alignment of the mesophase, since the side groups usually align perpendicular to the backbone (analogous to Warner's[6,7] nematic phase N_l), and this would be expected to ease the formation of a mesophase in which the side groups force the backbone to assume planar anisotropy.

A glance at the literature reveals a variety of surface preparations in use for both SCLCPS and SMLCS. The situation can be clearly illustrated by a selection of quotes:

> '. . . glass plates were treated with polyvinyl alcohol and then rubbed unidirectionally. Excellent planar samples were obtained after cooling down the [SMLC cyanobiphenyl] samples slowly (~1°C/min) from the isotropic state. [Reference 61]'

> 'The liquid crystal cell contained [ITO] electrodes covered by rubbed, antiparallel poly(hexamethylene) terephtalamide alignment layers [apparently producing a homeotropic SMLC smectic A texture] [Reference 59]'

> 'The planar anchoring [of a smectic A SMLC] . . . is obtained by evaporating silicon monoxide under oblique incidence onto the electrodes. The homeotropic anchoring . . . is reached by coating the electrodes with a thin layer of cetyltrimethylammoniumbromide. [Reference 67]'

> '[Homeotropic] orientation [of a smectic A SMLC] was produced by dipping the conducting pieces of glass in a solution of either lecithin in petroleum ether or hexadecyltrimethylammonium bromide in methanol. Homeotropic alignment has also been obtained on very clean glass surfaces, produced by cleaning and baking the glass at 450°C, or by electron beam deposited SiO_2 at 90° incidence. No doubt other surfactants such as dimethyldichlorosilane would also be effective. [Reference 58]'

> 'The [side chain] polymer samples were contained between two transparent conducting glass slides . . . No particular treatment was given to the glass substrates other than a thorough de-greasing followed by washing in isopropanol. [Reference 39]'

> 'The glass plates were subsequently rubbed by means of a styropor wheel to obtain a homogeneous orientation. The cell was filled using the capillary effect . . . . The [SCLCP] orientation was sufficiently good for the measurements, but nevertheless was not perfect along the rubbing direction. [Reference 45]'

> 'In comparison to the low molecular liquid crystals the orientation of the liquid crystalline side chain polymers is more complicated. A comparably good [planar?] orientation is achieved if the glass surface is coated with a thin film of polyimide. The quality of the orientation is better if it is attained by slow cooling of the liquid crystalline material rather than by a rapid temperature change. The latter mode of treatment leads to a destruction of the oriented layer. [Reference 20]'

> 'Initially the [smectic A SMLC] phase is aligned in a thin cell such that the structure of the phase has a uniform tilt of 68° from the glass surface (22° from the homeotropic direction). . . . The [smectic A] phase was aligned by evaporating SiO at a glancing angle of 5° onto flat indium-tin-oxide coated glass, and then dipping the SiO coated

electrodes into a dilute solution of hexadecyl trimethyl ammonium bromide in methanol and allowing them to dry. The SiO evaporation directions were placed parallel but opposite when the cell was assembled . . . [Reference 65]'

Coates *et al.*[58] compared the roughness of different commercially available indium-tin-oxide (ITO) coated glasses. The roughness of the surface had a significant effect on the scattering intensity of the disaligned smectic A SMLC sample, and the voltage required to initiate scattering due to instabilities (at low frequencies) was lower with rough surfaces. The explanation proposed is that the rough surface causes undulations in the smectic layer structure, which initiates scattering. They also found that rough surfaces slightly reduced the threshold voltage required to align the material (at high frequencies). Findlay *et al.* report that smectic A SCLCP samples showed better clarity after alignment if the ITO surface was baked[34] (and hence smoother, according to Coates[58]), and observe some homeotropic surface alignment of the side groups by ITO substrates.[3,4,30,34]

Surface alignment remains something of a black art despite the considerable effort which has gone into measuring anchoring strengths on various substrates using various techniques (see, for instance, Yokoyama's review[68] of nematic SMLC alignment). It seems that SCLCPs are not as strongly aligned by surfaces as their SMLC counterparts.

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