Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article McNamee, S. G. , Bunning, T. J. , Patnaik, S. S. , McHugh, C. M. , Ober, C. K. and Adams, W. W.(1995) 'The effect of electric and magnetic fields on the melt organization of a nematic cyclic siloxane liquid crystal', Liquid Crystals, 18: 5, 787 — 794

To link to this Article: DOI: 10.1080/02678299508036691

URL: http://dx.doi.org/10.1080/02678299508036691

LIQUID CRYSTALS, 1995, VOL. 18, NO. 5, 787–794

The effect of electric and magnetic fields on the melt organization of a nematic cyclic siloxane liquid crystal

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(*Received 5 May 1994; accepted 4 October 1994*)

The presence of periodic diffuse meridional reflections in the X-ray diffraction pattern of the nematic phase of a pentamethylcyclosiloxane compound with pendant mesogenic groups is examined as a function of temperature and frequency of an applied electric field. These reflections are thought to be caused by a tendency of the mesogens to pack in columns of molecules that have no side-to-side registry (uncorrelated strings). Column lengths obtained from the intercepts of plots of Δs^2 versus s^2, where s is the scattering vector and Δs is the width of the reflection, indicate association of 3–6 mesogens depending on temperature and frequency. The length over which the strings are correlated are compared to values obtained from a magnetically aligned sample quenched into a glassy nematic phase. The development of a pseudo-layered packing arrangement with decreasing temperature is also discussed. The appearance of a symmetric 4-spot pattern at temperatures slightly above the crystallization temperature suggests the formation of layered domains with local ordering similar to smectic C packing. Layer correlation lengths are calculated and compared for the electrically (110 Å) and magnetically (180 Å) aligned samples.

1. Introduction

Side-chain thermotropic liquid crystalline (LC) materials are being studied as candidates for application in electro-optical devices [1], non-linear optics [2, 3], and optical storage media [4, 5]. LC polymers as a class of materials have been very successful as high performance fibres and injection moulded components and are beginning to be used more in a variety of industrial applications, including ones where chemical resistance is needed and good wear resistance is desired in mechanical components [6]. A greater understanding of the development of the structure present within these materials during processing is desired. Most LC materials will align within applied electric and magnetic fields. This can translate the molecular anisotropy of the mesogens into a macroscopic anisotropy. However, under the influence of external fields these materials are not usually in thermodynamic equilibrium. Non-equilibrium conditions can lead to dramatically different arrangements of the mesogens with potential effects on optical, mechanical, and viscoelastic properties. We focus our attention on the use of applied electric fields to develop aligned LC structures.

The distinctive X-ray scattering of aligned LC phases has been used for many years as a method for identifying and probing the packing of anisotropic molecules. Many texts and reviews of X-ray scattering from LC polymers exist [7–9]; the definition and evaluation of molecular anisotropy in LC polymers has been particularly well developed by Mitchell and Windle [10]. By aligning the domains of the LC mesophase, the coherent scattering of X-rays from the material is increased and identification of the structure facilitated. Many researchers studying the electric field alignment of main-chain LC polymers have sought to observe the influence of temperature, applied voltage, and frequency by using dielectric relaxation spectroscopy (DRS) and polarizing optical microscopy (POM) [11, 12]. The DRS technique depends on certain assumptions about the electronic structure of the mesogens and POM yields information on the macroscopic scale. As a complementary technique, X-ray scattering looks at the physical arrangements of the mesogens with respect to their neighbours on the molecular scale. X-ray studies involving the effect of applied electric fields on LC systems until recently have been confined to side-chain LC polymers and to small molecules [13, 14].

For LC material applications where a low glass transition temperature is desired, linear siloxane polymers

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have seen considerable study. Coupling of the main-chain and side-chain motions is minimized by the flexibility of such a backbone. Recently, several groups have reported possible microphase separation of the hydrocarbon side-chain mesogens from the linear siloxane backbone based on X-ray diffraction results [15–17]. LC systems of increasing interest consist of small siloxane rings with various pendant mesogenic groups, for example, a mixed cyanoester and cyanobiphenyl system [18] or a mixed cholesterol–biphenylbenzoate system [19–21]. The material studied here is a model system for optically multifunctional [22] materials. These cyclic compounds are an advantageous combination of a glass forming material, which allows the LC order to be vitrified, and a low melt viscosity material, due to their low molecular weights ($\sim 2000\,\mathrm{g\,mol^{-1}}$), which facilitates processing. The dynamics of one such material's response to varying conditions of temperature and electric fields as observed via real-time X-ray scattering has been detailed elsewhere [23].

The combination of frequency addressable orientation typical of many low molar mass LC materials with the good mechanical and film-forming properties of polymers is of current technological interest, especially in the area of reversible information storage devices [14, 24]. Behaviour similar to the system in this study has been seen in linear LC polysiloxanes using dielectric spectroscopy [25–28] as well as optical techniques [26, 29]. Work with side-chain polyacrylates [30] and main-chain polyesters [31] using optical techniques exist, but to our knowledge, with the exception of our previous paper on the dynamics of this system [23], the observation of a frequency mediated structural change using X-ray scattering in real-time has not been previously reported.

The purpose of this paper is to describe our use of synchrotron radiation to probe the non-equilibrium, electric field mediated structures of the LC phase. Conventional X-ray sources, both fixed and rotating anode, do not have sufficient intensity to permit monitoring of microstructural changes in real time [32]. We have had success developing synchrotron techniques to observe dynamic structures in side-chain polymer liquid crystals [33, 34], and in novel liquid crystalline thermosets [35]. Given that the constituent atoms of the material have small scattering cross-sections for X-rays, it is only by using the high flux of radiation available from a synchrotron source that these dynamic and transient structures can be observed using X-ray scattering. As reported previously, a series of periodic, diffuse reflections were observed upon application of an electric field [23] in the nematic phase of a low molar mass cyclic siloxane compound. This work investigates the column lengths, the length of a one-dimensional array of mesogens calculated from the breadths of the periodic diffuse X-ray reflections, as a function of temperature and frequency. Layer correlation lengths are also calculated from a smectic-like reflection appearing at temperatures near the crystallization temperature. These are compared to values obtained from a magnetically aligned sample.

2. Experimental methods

The experimental protocol used was the same as reported previously [23] with few variations. The schematic of the electrode set-up is shown in figure 1. Diffracted radiation (monochromatic, 1·54 Å) was detected using flat-film (Kodak DEF). The transmission diffraction patterns were captured at a sample-to-film distance of 80 mm. Exposure times varied from 5 to 20 s depending on the flux of incident X-rays which was monitored using a N_2 ion chamber ($10\,\mathrm{cc\,mm^{-1}}$, 1 cm flight path).

A 100 V field was applied across a $100\,\mu\mathrm{m}$ gap at temperatures of 120°C to 170°C with frequencies of 1 Hz to 10 kHz. Typical procedures involved cooling from the isotropic phase to the desired temperature within the mesophase temperature range. The voltage was applied and changes in the smaller-angle reflection ($2\theta = 4°$) (where θ is the scattering angle) were observed using a video-rate detector (discussed previously [23]) until no further dynamic response could be observed. The video-rate detector was removed and a flat-film photograph was taken at this steady-state alignment. The sample was heated to the isotropic phase to eliminate any residual orientation and cooled to the next temperature. Because the thermal history of the sample can greatly affect the response of the sample to the electric field, and consequently the final organization of the melt, the degree of alignment was also monitored during cooling from 170°C to 120°C with applied frequencies of 10 Hz and 10 kHz. The cooling process was monitored in real-time using the video-rate detector and diffraction patterns were recorded

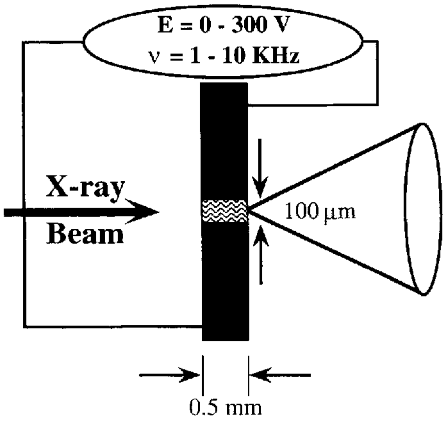


Figure 1. Schematic of electrodes used to electrically align samples showing the range of voltages and frequencies used.

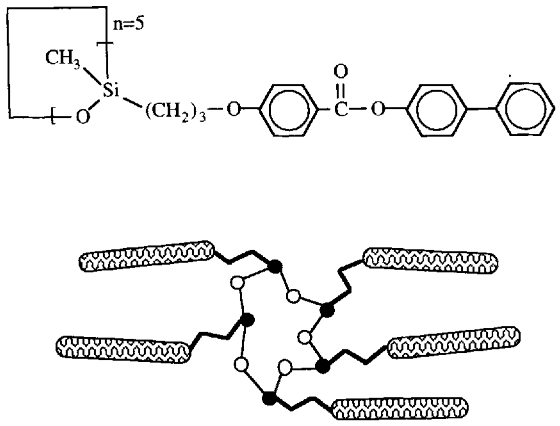
using flat-film at the lower end of the mesophase temperature range.

The X-ray film was analysed using a Molecular Dynamics Personal Densitometer equipped with a Mitsubishi Video-Copy processor. Orientation parameters were calculated as described previously [23]. Linear scans through the periodic, diffuse reflections were used to generate the column length information. Background information was obtained from linear scans from films with the same exposure time without the LC present. The data were corrected for the geometry of the experiment, Lorentz-polarization, and instrumental broadening of the X-ray beam. The data were analysed in terms of s as defined in equation (1). Full width at half maximum (FWHM) for the scattering peaks were measured and defined as Δs.

$$s = \frac{2\sin(\theta)}{\lambda}. \tag{1}$$

3. Results and discussion

The material under study, shown in figure 2 along with its transition temperatures, consists of a pentamethylcyclosiloxane core with attached biphenyl-4-alkyloxybenzoate side chains. Previous work on this compound has shown that it exhibits multiple orders of reflections along the meridian when electrically aligned with the nematic phase [23, 36]. Similar LC materials, including a conventional linear polysiloxane backbone with the same mesogen attached, did not exhibit such complex microstructural ordering within comparable fields. The microstructural ordering of the cyclic system in response to the electric field is complicated by the system's frequency dependent dielectric anisotropy, which causes the director to undergo a 90° rotation with respect to the electric field at high frequencies [23].



Heating: C_1 115 C_2 135 N 175 I
Cooling: I 175 N 112 C

Figure 2. Chemical structure, schematic and thermal transitions of the material used in this study.

Examples of the complex diffraction patterns obtained from this system aligned at various frequencies can be seen in figure 3. Even within a few degrees of the clearing temperature, the system exhibits periodic diffuse reflections along the meridian (parallel to the electric field direction) regardless of frequency. Four or five periodic reflections with a primary spacing of approximately 23 Å are observed depending on the temperature and frequency. At 120°C, approximately 10° above the crystallization temperature of the material, alignment along the meridian occurs at 10 Hz but a switch in orientation is observed at 10 000 Hz. Multiple orders of reflections are then evident along the equator instead of the meridian. The spacings did not change appreciably upon reorientation. This switch in orientation occurs below 145°C and only occurs progressively with lower frequencies as the sample is cooled [23]. The unaligned sample shows no sign of these diffuse reflections as shown in figure 4. A large wide angle halo at 4–6 Å characteristic of the side-to-side interactions present in a nematic phase is clearly evident.

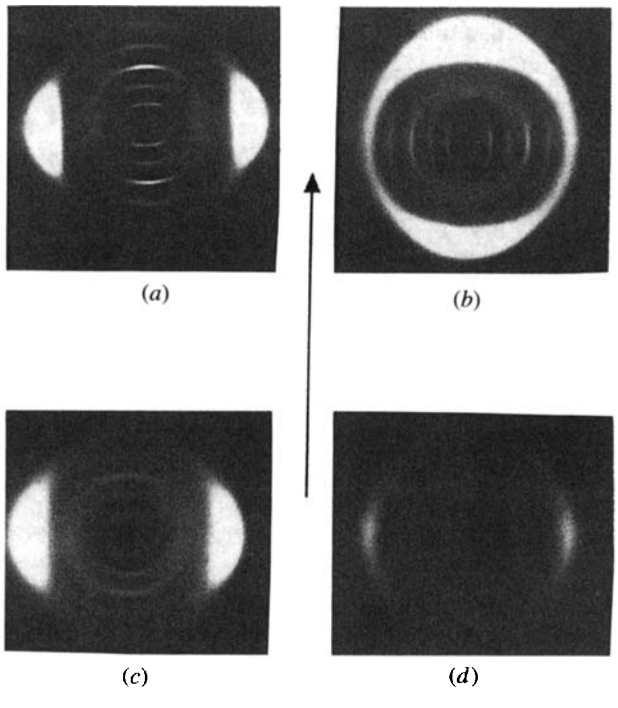


Figure 3. Diffraction patterns from the LC sample within the electric field (a) at 120°C and 10 Hz, (b) 120°C and 10 kHz, (c) 170°C and 10 Hz, and (d) 170°C and 10 kHz. Direction of the electric field is indicated by the arrow and is constant for all photos. The large crescents are centered at a spacing of 4–5 Å. Orthogonal to these crescents, a series of periodic diffuse reflections exist with the inner most reflection having a spacing of 23 Å.

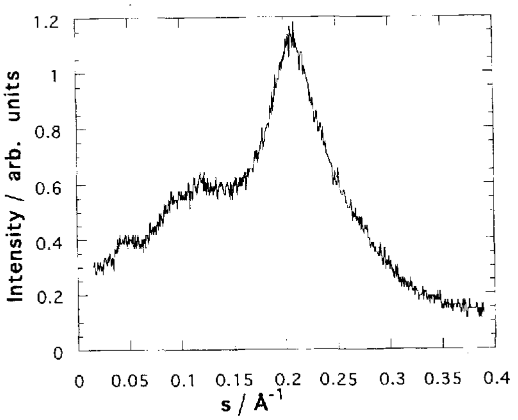


Figure 4. Meridional scan through the film taken of the material in the unaligned nematic state at 140°C.

The nature of the periodic reflections along the meridian (or equator, depending on frequency) is not simple and warrants discussion. For smectic LC polysiloxanes, it has been observed that the electron density of the backbone can lead to a large number of Bragg reflections due to the smectic layers as compared to other polymers such as polyacrylates or polymethacrylates [15]. The system under consideration, however, exhibits only nematic textures under POM, and would not be expected a priori to exhibit such scattering. The meridional reflections can be described as straight, equidistant diffuse streaks with well-defined periodicity along the director of the system. The geometry of the reflections, shown schematically in figure 5, is similar to that of a Fourier transform of a linearly modulated object oriented along the director [37]. The columnar system in real space has a periodicity of d along the director, **n** similar to main chain LCPs. The Fourier transform of this packing geometry is parallel lines perpendicular to **n** whose spacing is inversely proportional to the repeat distance (*d*) and whose thickness is inversely proportional to the distance over which association occurs (*L*). The term column length is used to represent this distance in discussions below. One can interpret this physically as indicating the mesogens tend to align themselves in one-dimensional columns over short distances. The length of these columns may be estimated from the width of the reflections measured from the X-ray photos.

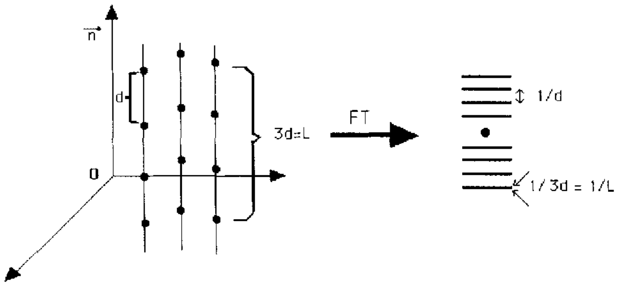


Figure 5. A schematic representation of a columnar system in real space with its Fourier transform (not to scale).

The breadth of the reflections, Δs, determined from the full width at half maximum of the intensity, can be used to calculate the distance, *L*, over which the mesogens are correlated. Three factors can contribute to the broadening of the periodic diffuse reflections. Both variation in the size of the scattering domains (scatterer size) as well as thermal fluctuation of the atoms about their equilibrium lattice positions (type *I* disorder) will impart a Cauchy shape to the X-ray reflection. All other disorder (type *II* disorder) within the material will lead to a Gaussian shaped reflection [38]. The scattering from a real crystalline material will have components of both shapes. Our samples (liquid crystalline) were expected to exhibit considerably more disorder compared to a solid crystalline material and therefore a Gaussian line shape was used to best fit the scattering data. For Gaussian distributions, the average size of the scatterer (column length) can be obtained from the intercept of the best fit line on a plot of Δs^2 versus s^2 [39]. The intercept corresponds to the reciprocal of the square of the column length, *L*.

Figure 6 shows the Δs^2 versus s^2 data for the sample obtained from steady state alignment (cooled without field) at 120°C at 10 Hz and 10 000 Hz. It should be noted that the data for the 10 000 Hz case was obtained from a linear scan through the equator due to the switch in orientation that had taken place, as shown in figure 3 (*b*). The scattering pattern was recorded after the field had been applied and a steady-state alignment had been achieved. The intercept for the 10 Hz case corresponds to $L = 124$ Å indicating approximately 5 repeat units are associated in a column (see figure 5). The value for the 10 000 Hz case was slightly lower at 106 Å. Figure 7 shows the data for the same two frequencies when the material was cooled at

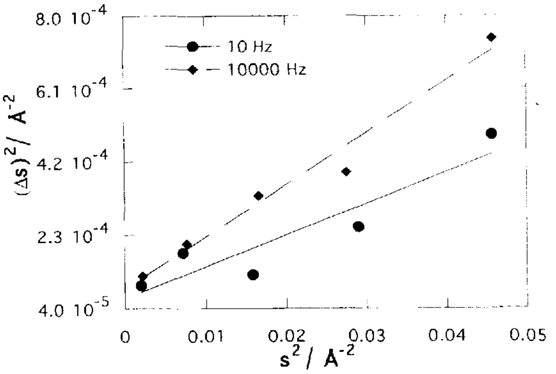


Figure 6. The FWHM of the periodic, diffuse reflections for the material aligned with 10 Hz and 10 kHz fields at 120°C.

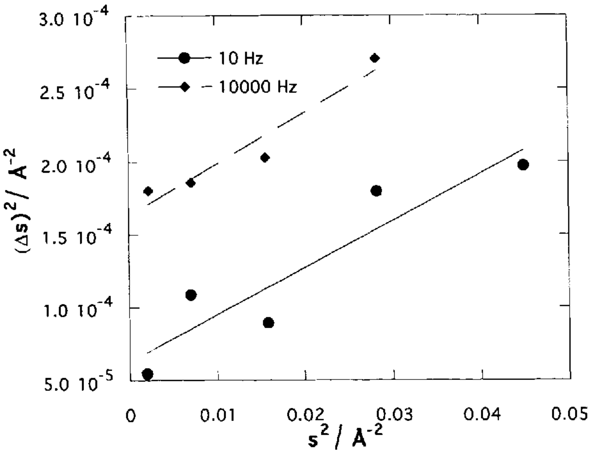


Figure 7. The FWHM of the periodic diffuse reflections for the 10 and 10 kHz frequencies after cooling from the isotropic state to 120°C with the field applied.

10°C min^{-1} from the isotropic phase to 120°C with the field on. The value of $L = 127$ Å for the 10 Hz case suggests little difference in the degree of association was induced by cooling with the field applied. This was not the case for the 10 000 Hz run as a much smaller value of $L = 78$ Å was obtained when cooled to 120°C with the field on, corresponding to an association of only 3 repeat units. This implies that while cooling, destruction of the column-like association occurs when reorientation takes place below 145°C.

This destruction can be clearly seen when the column lengths obtained from steady state alignment are plotted as a function of temperature as shown in figure 8. For the 10 000 Hz frequency, the column length is fairly constant at approximately 80 Å when cooled from the isotropic state to 150°C. At 140°C, slightly below the temperature where reorientation takes place, the column length decreases substantially to $L = 44$ Å. Steady-state alignment at the lower temperatures yields increasing values of L. The low value ($L = 78$ Å), obtained when cooling with the applied field, is attributed to the decrease in the amount of association when reorientation takes place. The higher value (106 Å) observed when the 10 000 Hz field was applied after the material was cooled to 120°C is the result of an equilibrium alignment being formed. The kinetics to achieve this steady-state alignment have been documented previously [23]. The cooling run samples were allowed to equilibrate at 120°C which indicates the low degree of association obtained in the 10 000 Hz case is not a transient value.

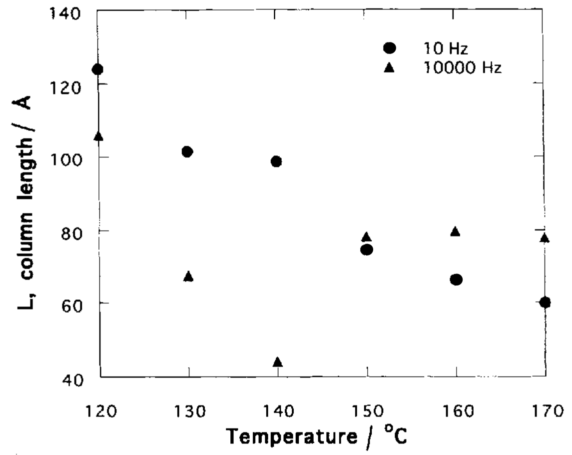


Figure 8. Calculated column lengths, L, for both 10 Hz and 10 000 Hz throughout the mesophase temperature range for steady state alignments.

The column lengths for the 10 Hz frequency steadily increase with decreasing temperature from a value of $L = 60$ Å near the isotropic state to a value of $L = 124$ Å at 120°C, shown in figure 8. This can be contrasted with relatively small changes of the orientation parameter through the same temperature range as shown in figure 9. The ability to do real-time scattering with high X-ray flux is advantageous as both molecular and domain structure information can be obtained as a function of time. Bulk order parameter measurements as obtained with POM do not yield information about the molecular organization of ordered phases. Similarly, conventional diffraction techniques would not allow for a real-time investigation of structural rearrangements and structure development as previously demonstrated [23].

The degree of association induced by the electric field can be compared to that obtained from a magnetically aligned sample. The details of the alignment procedure have been reported elsewhere [40]. The meridional linear scan, shown in figure 10(*a*), indicates 6 periodic reflections are present. The molecules align parallel to the magnetic field direction analogous to the 10 Hz electrically aligned samples. The intercept of the Δs^2 versus s^2 plot shown in figure 10(*b*) indicates a column length of

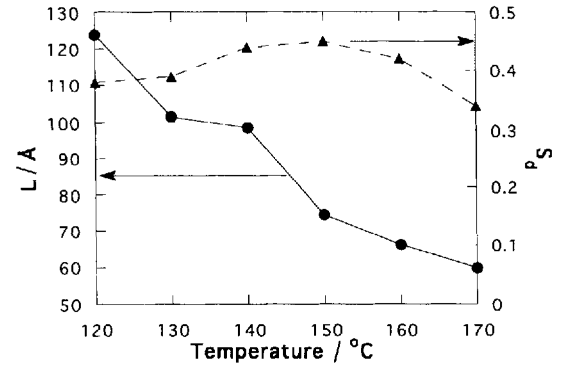
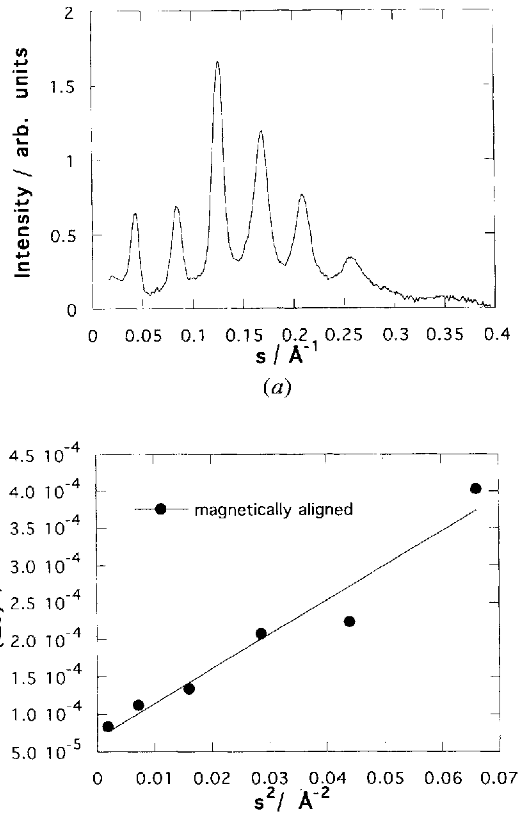


Figure 9. Comparison of the change in the column length of the system with temperature to the relatively fixed degree of orientation.



(*a*)

(*b*)

Figure 10. (*a*) Meridional scan of the magnetically aligned sample. (*b*) The FWHM of the periodic, diffuse reflections for the magnetically aligned sample versus reflection position.

$L = 121$ Å, similar to the values obtained at 120°C. A larger value was expected as the diffraction pattern was more ordered and the meridional reflections looked narrower. Indeed, analysis of the wide-angle scattering indicates an order parameter of 0·76 which is considerably higher than the value of approximately 0·4 at 120°C.

A symmetric 4-spot Bragg pattern centre about the meridian was observed when the material was aligned at the lower temperature (120°C) using a 10 Hz field. This effect was much more dramatic in the magnetically aligned sample as indicated by the sharpness of the 4-spot pattern off the meridian as shown in figure 11. The sharpness of the reflection is an indication that a layer-like structure is being formed. A tilt angle of 43° was obtained from both magnetically and electrically aligned samples. These split reflections off the meridian are an indication of the formation of cybotactic groups (domains with local smectic C ordering) [41]. This splitting, while it occurs when the system is aligned isothermally, is much sharper and more intense for samples cooled with the field applied at 10 Hz. If cooled below 120°C, the material crystallizes and the alignment initially present is lost. This indicates that the electric field may increase the crystallization temperature relative to an unaligned sample.

No indication of the 4-spot pattern is observed when aligned at 10 000 Hz. The columnar nature of the one-dimensional packing of mesogens remains however, as demonstrated by the multiple reflections along the equator. As stated before, there is no indication that this system is anything but nematic when examined via POM of differential scanning calorimetry (DSC). The unaligned X-ray scattering is also typical of a nematic melt. Only the aligned X-ray scattering pattern appears to be from a system that is not a traditional nematic. Observing a phase or a phase change within an LC system via X-ray scattering that is incommensurate with other measuring techniques is not without precedent [42–44]. Smectic C phases, when aligned, can show a splitting of the first order reflection about the meridian. Only the first-order split reflection is observed for this system indicating very long range order is not present. This is consistent with the material still exhibiting a nematic phase. It should be noted

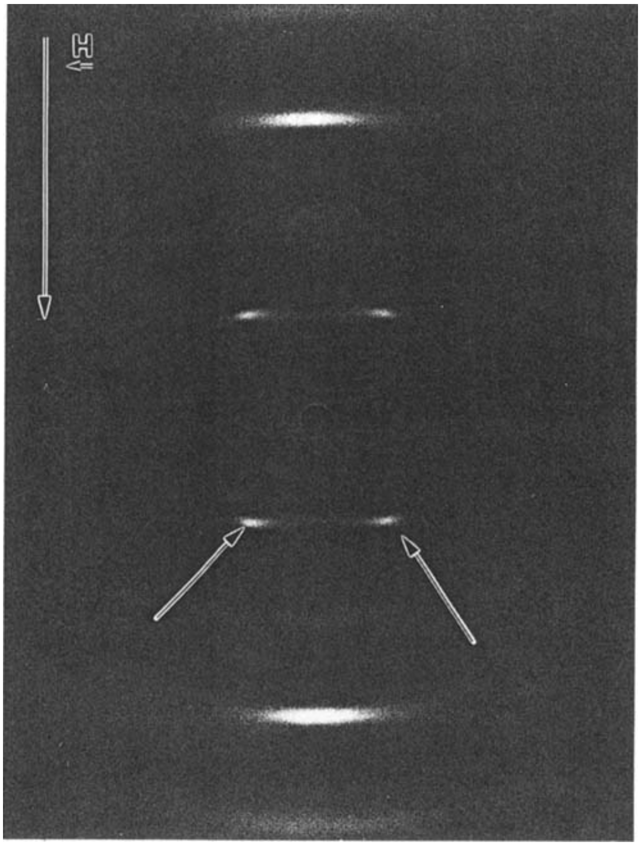


Figure 11. Diffraction pattern from the magnetically aligned sample showing split 4-spot pattern off meridian which develops at temperatures near crystallization. These spots are superimposed on the first diffuse reflection which has a spacing of 23 Å. The vertical arrow indicates the direction of *H* field.

that an analog to this nematic system in which the spacer between the mesogen and the cyclic siloxane backbone consists of a 5-carbon chain instead of a 3-carbon chain, does exhibit a monotropic smectic C mesophase from 125°C to 105°C, as observed using POM [21]. Perhaps the compound used in this study is a virtual [45–47] smectic C material, which crystallizes before the smectic phase can fully develop, and the effect of the electric field is to drive up the LC transition temperature.

Whereas little difference in the column lengths was observed between magnetically and electrically aligned samples, a larger difference was observed for the layer correlation lengths. In order to understand the origin of the smectic-like behaviour in these nematic liquid crystals, the layer correlation length was calculated using the Scherrer equation typically used to calculate crystallite sizes [39]. The integral breadth of these split, layer reflections were measured radially (at an angle of 43°). A correlation length of 180 Å was calculated for the magnetically aligned sample. This degree of correlation is unusual for a material exhibiting only a nematic phase. The electrically aligned sample cooled with the field applied exhibits a layer correlation length of 110 Å. Data obtained from the samples isothermally aligned with the 10 Hz field could not be analysed in this fashion as the 4-spot pattern was weak in intensity.

Based on these results a simple packing model can be postulated as shown in figure 12. In the nematic phase, the material has a propensity to form one-dimensional columns with lengths ranging from 3–6 mesogens with no lateral correlation. At temperatures near the crystallization temperature upon cooling, a smectic C-like phase is formed where the tilt angle is approximately 43°. A large layer correlation length in this tilted mesophase as estimated by the Scherrer equation is induced by application of an applied field. Similar diffraction patterns have recently been reported for a series of Siamese-twin compounds exhibiting low molecular weight glassy mesophases [48]. The type of packing postulated in this work is very similar to that postulated for this cyclic siloxane shown in figure 12.

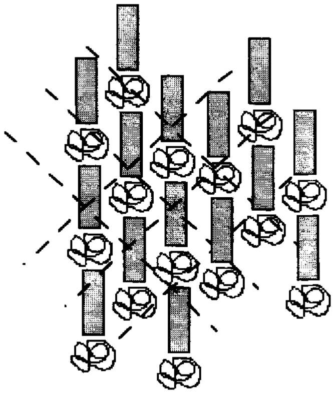


Figure 12. Schematic of possible packing arrangement of the calamitic mesogens and the siloxane backbones under the influence of an applied electric field. Dashed lines are to aid the eye.

4. Conclusions

We have seen that by adjusting the frequency of an applied electric field, one may address frequency dependent dielectric anisotropies that exist within a liquid crystalline material and thereby produce mesomorphic melts with very different levels of order. Such observations can now be made using X-ray scattering to directly observe the structures involved during molecular rearrangements. While this frequency dependence has been the basis of much of the technology surrounding small molecule liquid crystals, it is hoped that it will prove useful to the development of new technologies using polymer liquid crystals as well.

For this system of a cyclic siloxane liquid crystal, orientational order and column length during electric field alignment are not correlated. The scattering from the nematic phase exhibits diffuse but intense meridional streaks indicating columnar packing under the influence of an aligning field. The lengths of these columns are affected more by sample temperature than the frequency of applied field. Column lengths range from 6 down to 3 mesogens, and are shorter at the higher temperatures because of the increase in the thermal energy randomizing the position of near-neighbour mesogens. Magnetically aligned samples exhibit similar values for column lengths although exhibiting much better alignment.

At low temperatures, a 4-spot small-angle Bragg diffraction pattern is seen which suggests formation of a weak smectic C-like phase. The sharpness and intensity of these spots, like most of the characteristics of liquid crystalline systems, are greatly affected by thermal history. A simple model of the packing scheme has been proposed based on the interpretation of the available X-ray data.

Thanks to E. Karikari for his assistance and E. T. Samulski for magnetically aligning the 5-member ring sample. Thanks also to the Materials Science Center and the Cornell Energy Synchrotron Source (CHESS) for use of their facilities. The authors greatly appreciate their discussion with D. Grubb and Ya. Freidzon. Funding by the NSF and the American Chemical Society administered Petroleum Research Fund is gratefully acknowledged. S.G.M. wishes to thank the Department of Education for a graduate fellowship. T.J.B. acknowledges support from an Air Force contract, F33600-95-C-0055.

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