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Probing the electric field alignment of a thermotropic liquid crystalline polymer by synchrotron radiation

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The orientation of a cyclic side-chain thermotropic liquid crystalline material in an AC field was monitored in real-time using synchrotron radiation. Monitoring the realignment processes in the millisecond-to-minute time-scale was made possible by the high X-ray flux. Orientation parameters and response times were calculated as a function of temperature and frequency. Response times decreased exponentially with temperature due to a decrease in the viscosity. Very little dependence of the response time on frequency was observed, except at low temperatures, where a switch from homeotropic to planar alignment of the molecules was detected. This reorientation of the director was studied in real-time and the resulting complex diffraction patterns were due to equal but opposite director rotations from an alignment parallel to the applied electric field to an alignment perpendicular to the applied electric field. The orientation parameters were highest in the central portion of the mesophase temperature range. At temperatures near clearing, the net degree of orientation diminished. Cooling through the mesophase with an applied electric field resulted in much larger orientation parameters than could be obtained by aligning at a fixed temperature in the mesophase.

1. Introduction

The orientation of low molecular weight (LMW) and polymeric liquid crystalline materials with an applied electric or magnetic field is a well-known phenomenon [1]. Coupling of the electro-responsive and magneto-responsive properties of the LMW mesogens with the robust physical properties of polymeric systems is advantageous for many applications. The ability to align macroscopically and then vitrify order into the glassy state provides a method of introducing spatial contrast into thin films which is useful for applications such as data storage and display devices. Reversibility can be obtained by heating above the glass transition temperature, thereby 'erasing' the contrast. For electric-field alignment, differences in the dielectric anisotropy as a function of frequency and temperature are typically used to induce planar or homeotropic orientation of the director with respect to a substrate [2]. The strong dependence of the dielectric constants of polar mesogens on frequency allows for switching between the two orientations.

A number of ways of probing the director alignment have been used, including polarized light optical microscopy [3–5] and dielectric spectroscopy [6, 7]. Neither method yields molecular-based structural information on the organization of the LC

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phase, although both techniques are ideally suited for LMW systems where the response times are typically fast (< 1 ms). Static X-ray diffraction techniques have been used extensively to investigate the degree of order and molecular packing of the mesogens after alignment [8,9]. Because the response times of polymer liquid crystalline compounds are typically 10 to 1000 times higher (millisecond-to-minute scale) due to the increased viscosity of the materials, X-ray experiments on these systems cannot yield time resolved information about the alignment kinetics and structural transformation due to the long exposure times needed with ordinary X-ray sources. These conventional diffraction techniques can yield structural information on systems that align over hours or days [10]. Changes in orientation over short time scales can be obtained using NMR techniques [11] for alignment induced with magnetic fields.

We report here on AC electric-field induced alignment of a side-chain thermotropic liquid crystalline compound. The high flux of radiation from a synchrotron source allows for time resolved X-ray diffraction (TRXRD) experiments to be performed on this system where alignment occurs over millisecond and greater time-scales. Alignment response times and orientation parameters were obtained as a function of temperature and frequency. Changes in orientation were recorded in real-time using an image intensifier and digital camera to capture the diffraction pattern on video tape. Differences in orientation (planar versus homeotropic) were examined as a function of voltage, frequency, and cooling rate. Our experimental protocol is different from the usual investigation of the effects of applied fields on liquid crystalline materials. Instead of probing the material parallel to the applied field, as in polarized light optical microscopy, we are investigating the material perpendicular to the applied field. Within the context of our experimental geometry, the term 'homeotropic' refers to the arrangement of the mesogens parallel to the applied field and perpendicular to the electrodes, while 'planar' represents the arrangement of the mesogens perpendicular to the applied field and parallel to the electrodes (see below). Domain rotation and rearrangement during frequency mediated reorientation, referred to as 'switching', were also investigated as a function of time. Further analysis of the data reported here includes quantification of the structural correlation lengths present on the molecular scale [12]. This type of analysis is not possible with optical experiments as only macroscopic changes in structure are probed. A detailed report of this study of the molecular packing of the system under the influence of an applied field will follow in a future publication.

2. Experimental methods

X-ray diffraction data were obtained at the A1 beamline of the Cornell High Energy Synchrotron Source (CHESS). Sample cells consisted of two 0.5 mm gold-plated stainless steel electrodes separated by a controlled gap spacing of 100–200 μm (see figure 1) which were held in a Mettler FP 82HT hotstage. Samples were melted between the electrodes and held in place by capillary forces. Voltage and frequency of the applied field were controlled by passing the output from an HP 3300A function generator through a high voltage operational amplifier (Trek, model 10/10). Diffracted radiation (monochromatic, $\lambda = 0.154$ nm) was detected using an image intensifier coupled to a digital video camera. Scattering patterns were collected and stored on U-matic format video tape for storage and subsequent analysis. The collected solid angle of radiation of the image intensifier was small (2θ : 0 – 6°) and typically only the small-angle reflection (2θ : 3 – 8°) was fully recorded. Flat-film (Kodak DEF) was used to

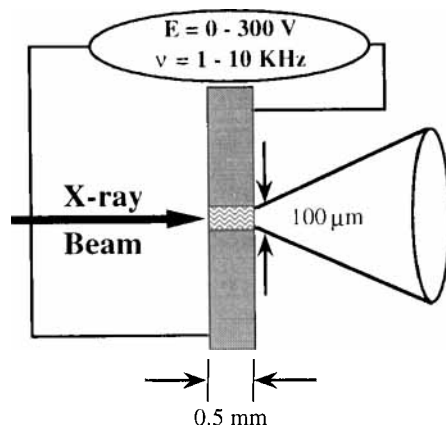


Figure 1. Schematic of electrodes showing the range of voltages and frequencies used.

record selectively the entire diffraction pattern (typically 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 cc min^{-1} , 1 cm flight path).

The material under study, shown in figure 2 along with its transition temperatures, consists of a pentamethylcyclorosiloxane core with attached biphenyl-4-allyloxybenzoate side chains. Previous work on this compound indicated a dramatic change in the degree of alignment with application of an electric field [13] over a limited range of frequencies and temperatures in the nematic phase. Similar LC materials, including a conventional linear polysiloxane backbone with the same mesogenic unit attached, did not respond with comparable field strengths. Since a strong dipole is not present in this LC compound, the marked alignment of the cyclic siloxane system in electric fields was unusual.

To map the response of the material fully in the nematic phase, a more detailed examination was undertaken. A 100 V field was applied at temperatures of 120–170°C with frequencies of 1 to 10 000 Hz. Typical procedures involved cooling to the desired temperature from the isotropic phase. The voltage was applied and changes in the small-angle reflection were recorded on the video tape until no further changes could be seen. The image intensifier was removed and a flat-film photograph was taken at this steady-state degree of alignment. The image intensifier was replaced, the field turned off, and the relaxation was monitored on video tape (only alignment data will be discussed here). The sample was heated to the isotropic phase, to clear the thermal history, and cooled to the next temperature. The degree of alignment was also monitored during cooling runs from 170°C–120°C at 10 000 and 10 Hz. The cooling process was monitored in real-time using the image intensifier and the resulting diffraction pattern was recorded on flat-film photographs. Several cooling rates were examined.

An RCI Framestore image processor was used in conjunction with a commercially available image processing software package to analyse the digitized data. Data sets in the form of intensity versus x, y pixel position were captured as frames from the videotape. A data set could be obtained at video rates (1/30 s), the time resolution limit for this system. Resolution of the diffraction data was 10 milliradians at the sample-to-detector distance employed, similar to previously reported techniques [14]. Meridional and equatorial radial scans were taken from the small-angle reflection at various times after the field was turn on. After correcting for the background and

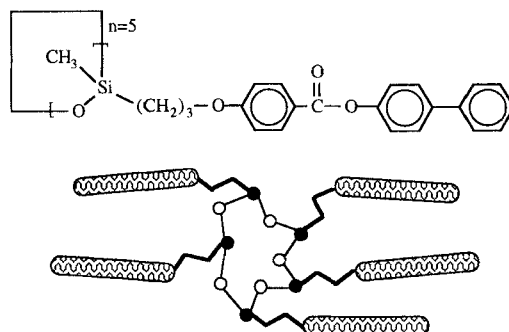


Figure 2. Chemical structure, schematic, and thermal transitions of the material used in this study. Heating: C₁ 115 C₂ 135 N 175 I. Cooling: I 175 N 112 C.

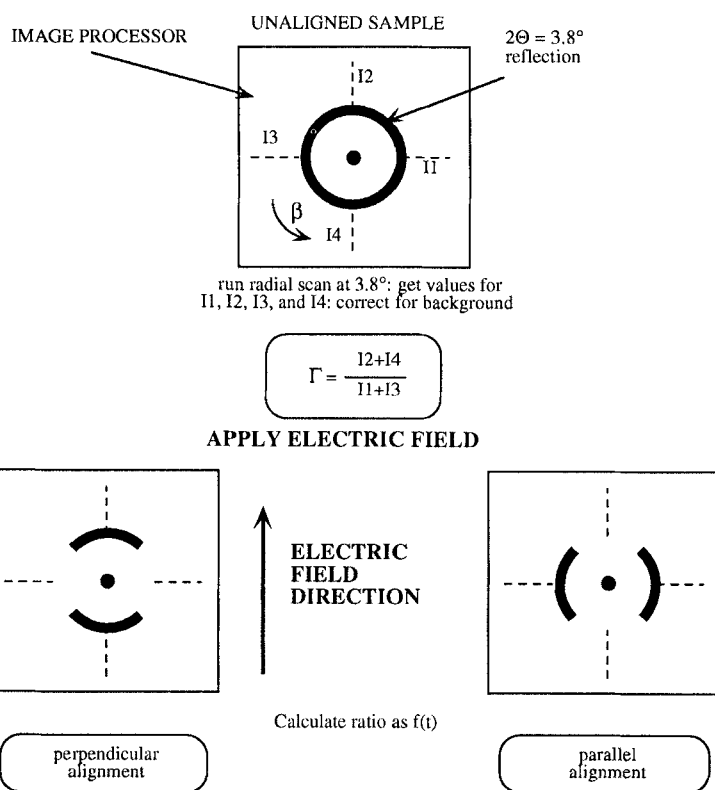


Figure 3. Summary of the measure of alignment using the image intensifier.

differences in incident flux, the meridional data were divided by the corresponding equatorial data to give a measure of the alignment as a function of time (shown schematically in figure 3).

Orientation parameters were calculated from azimuthal scans passing through the wide-angle reflections on the flat-film. Background azimuthal scans at the same 2θ angle were subtracted after correcting for differences in incident flux. The distribution in intensity (I) as a function of angle (β) for a given quadrant of the azimuthal scan was obtained (see figure 3). Peaks in intensity were made to reside at an angle of $\beta = 90^\circ$.

Conversion of the $I(\beta)$ data to $I(\alpha)$ is accomplished using the relationship from spherical trigonometry shown in equation (1)

$$\cos(\beta) \cos(\theta_B) = \cos(\alpha), \quad (1)$$

where θ_B is the Bragg angle and α is the angle between the normals to the scattering planes and the electric field direction. To calculate the average cosine squared of α , integration of the $I(\alpha)$ data versus α is performed using equation (2) [15]

$$\langle \cos^2 \alpha \rangle = \frac{\int_0^{2\pi} I(\alpha) \cos^2(\alpha) \sin(\alpha) d\alpha}{\int_0^{2\pi} I(\alpha) \sin(\alpha) d\alpha}. \quad (2)$$

From geometry, we know that the summation of the average angles between the x , y , and z axes and the director must equal 1. If we assume cylindrical symmetry about the long axis of the molecules, one can relate $\langle \cos^2 \alpha \rangle$ to the average angle of interest, $\langle \cos^2 \varphi \rangle$, the average angle between the axis of the structural unit and the director using equation (3) [15].

$$\langle \cos^2 \varphi \rangle = 1 - 2\langle \cos^2 \alpha \rangle. \quad (3)$$

The director orientation parameter, S_d , is calculated using equation (4).

$$S_d = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (4)$$

Orientation parameters reported are the average of the four orientation parameters calculated for each film, one from each quadrant.

3. Results and discussion

Figure 4 shows the diffraction patterns of the sample at 120°C under no electric field (a), aligned at 10 Hz (b), and aligned at 10 000 Hz (c) within a field of $1 \text{ V } \mu\text{m}^{-1}$. The diffraction patterns consisted of wide-angle crescents at scattering angles characteristic of the average lateral packing distance of the mesogenic side chains. Orthogonal to these wide-angle reflections were reflections characteristic of the average length of the mesogen units. The complexity of the diffraction patterns (consisting of up to 6 meridional reflections and a 4-spot pattern shown in figure 4(b)) is unusual for a nematic and implications for the molecular packing of this material under the influence of an electric field will be discussed in more detail in a future publication. At 10 Hz, the molecular director is parallel to the E -field direction and corresponds to homeotropic alignment of the mesogenic groups relative to the electrodes. At the higher frequency, however, a switch in orientation was observed as the director became perpendicular to the E -field direction. In this planar orientation the mesogenic groups are parallel to the electrodes as indicated by the WAXS reflections. This switch in orientation is due to the frequency dependence of the dielectric anisotropy, $\Delta\epsilon$ [2]. Orientation parameters are reported as positive for the homeotropic orientation and negative for the planar orientation. Although values were calculated relative to the molecular director in each case (and not relative to the E -field direction), negative values for planar orientations were used to indicate that a switch from the predominant homeotropic orientation relative to the electrodes had occurred.

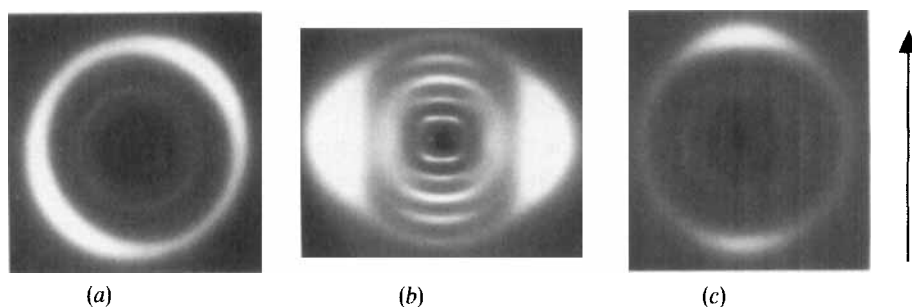


Figure 4. Flat film X-ray diffraction results of sample at 120°C unaligned (a), aligned with the field applied at 10 Hz (b), and aligned with the field applied at 10 000 Hz (c). Electric field applied in direction of arrow.

Director orientation parameters as a function of either temperature or frequency are shown in figures 5(a) and (b), respectively. The direction of orientation rotated through an angle of 90° at temperatures of 120, 130, and 140°C for 10 000 Hz and at 120°C for 100 Hz as indicated by the negative values of S_d as shown in figure 5(a). Planar orientation at 10 000 Hz increases as temperature is decreased, as indicated by the larger (negative) values for S_d . Further examination of the dependence of this switching at lower temperatures was inhibited due to crystallization. The frequency dependence of S_d at a given temperature, shown in figure 5(b), is weak through the mesophase region except at temperatures where switching occurred. Very little difference in S_d was observed from 150 to 170°C with frequency changes, except at 170°C and 1 Hz where S_d is substantially lower than values observed at other frequencies. At 120°C, the frequency at which switching occurred moved an order of magnitude lower than at 130°C. Once switched, the S_d values were substantially lower in absolute magnitude than before switching.

For the electric fields used in this study, orientation parameters ranged from 0.3 to 0.55 with the highest values being observed in the middle of the mesophase range (140°C and 150°C). For a given frequency, the orientation parameter first increased and then decreased as temperature was increased as shown in figure 5(a). This was true even at the high frequencies where switching had occurred. The lower orientation parameters at lower temperatures can be attributed to an increase in the viscosity of the mesophase such that the mesogenic side chains are not as free to respond to the applied field. The loss of order at higher temperatures is consistent with Maier-Saupe theory, in that the thermal fluctuations within the system overwhelm the ordering fields as T_i is approached.

The magnitude and kinetics of the steady-state orientation parameter in a DC field is governed by the equations of motions which dictate the realignment of LC molecules [16–18]. There is a balance between the dielectric torque imposed on the domains by the E -field and elastic torques which oppose it. Steady state alignment can be achieved when the competition among these forces is balanced. Response curves calculated in such a manner often exhibit a two-part response whose relative contributions to the transient S_d change depend on the balance of physical parameters. Very large initial contributions to S_d occur when the viscosities are low and the electric field strengths are high. Variations in the elastic constants also affect both the resultant degree of orientation and the response times. Reorientation processes begin as pure bend

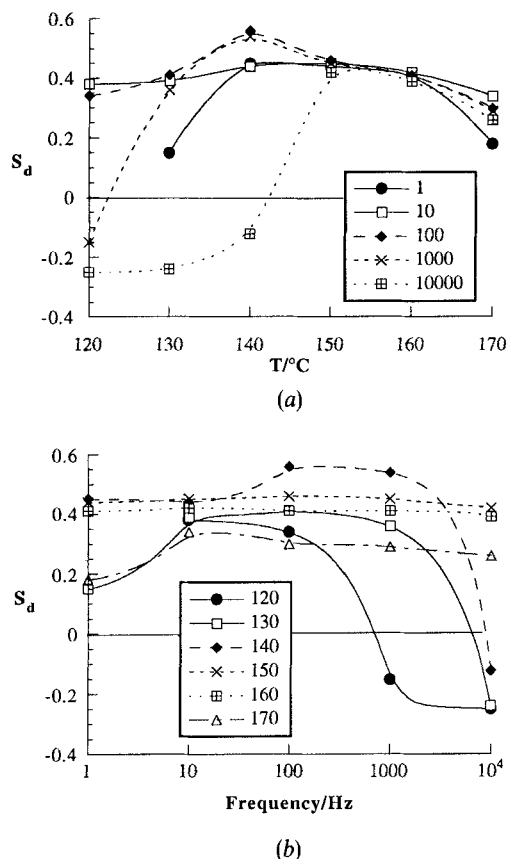


Figure 5. Director orientation parameters as a function of temperature (a) and frequency (b).

deformation of the mesogens followed by a gradual transformation to a splay deformation [16].

The experimental response curves observed in this study also exhibit a two-part response, an initial fast alignment process followed by a second, slower alignment process. Although we are using an AC field, we observe responses to the field similar to those associated with a DC field: increasing alignment until steady state is obtained. It is possible that the induced dipoles within the system cannot respond as quickly as the frequency of the AC field. In twisted nematic field effect (TNFE) mode liquid crystal cells, this phenomenon is called the accumulation of electric energy in the cell [2].

The response times to achieve steady state orientation were calculated by fitting the data sets collected with the image intensifier to equation (5).

$$\Gamma = m_1 + m_2(1 - \exp(-t/\tau_r)) \quad (5)$$

This is a variant of the standard equation used to fit conventional response time data from light microscopy measurements [1] with m_1 corresponding to the $t=0$ value, m_2 a measure of the steady state change in Γ (as defined in figure 3), and τ_r corresponding to the response time of the system. The value of τ_r therefore corresponds to a characteristic response time for a given frequency and temperature. Examples of the data for both orientations and the fitted curves that were used to obtain the τ_r values are shown in

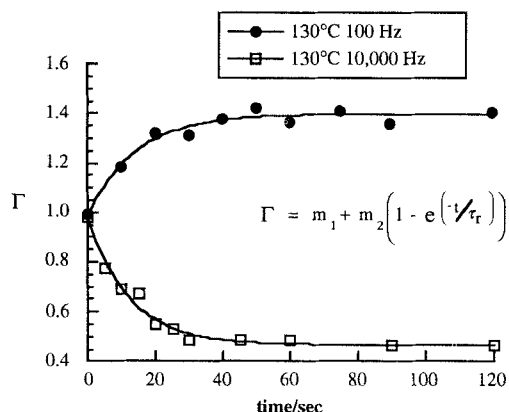


Figure 6. Typical time-resolved data and the fitting equation used to determine τ_r .

figure 6. For homeotropic alignment, the meridional intensity grows at the expense of the equatorial intensity and therefore Γ increases as a function of time. For planar alignment, the opposite response occurs yielding Γ values which decrease with time after the voltage is applied. The rate at which the sample is able to align increases markedly with temperature as shown in figure 7. The response times spanned several orders of magnitude from tenths of a second to several tens of seconds depending on temperature.

These switching dynamics from a planar to a homeotropic alignment in conventional LMW cells are dictated by equation (6)

$$\frac{1}{\tau_r} = \frac{k_{11}}{\eta_1} \left(\frac{\pi}{d} \right)^2 \left(\left(\frac{U}{U_0} \right)^2 - 1 \right), \quad (6)$$

where U_0 is the threshold voltage, U is the voltage, d is the sample thickness, k_{11} is the splay constant, η_1 is the viscosity, and τ_r is the response time. For this work at constant voltage, the response time should be proportional to the ratio of the splay constant to the viscosity. Since the viscosity is expected to decrease exponentially with increasing temperature and the elastic constant typically decreases linearly with temperature, one would expect the response times to decrease exponentially with increasing temperature. This is the case as shown in figure 7. Similar to the S_d values, there is little dependence of the response times on frequency for a given temperature.

The high flux of the synchrotron source allowed for transient structures present during the orientation processes to be examined. When the material was cooled from 170°C to 120°C at 10 Hz, an increase in the orientation parameter was observed (see figure 8). The final value at 120°C (0.56) was substantially higher than when the field was turned on at 120°C and the system allowed to equilibrate (0.38). By cooling from elevated temperatures, barriers to realignment are overcome which inhibit alignment at the lower temperatures. Thus, proper processing conditions can lead to substantial increases in the degree of orientation. Upon cooling with a frequency of 10 000 Hz, a switch from a positive to a negative S_d value was observed between 150°C and 140°C, corresponding to a change in the orientation of the molecules. Again, the S_d value obtained was larger after cooling with the field than when aligned at the lower temperatures. There was no trend in the final orientation parameter at 120°C with cooling rate. The cooling rate did affect the temperature at which the cross-over from

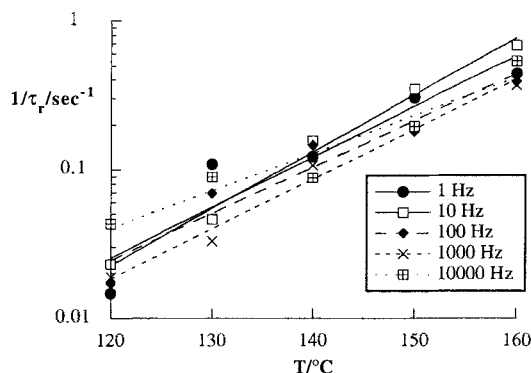


Figure 7. The rate at which the system is able to respond to the applied frequency increases markedly with temperature.

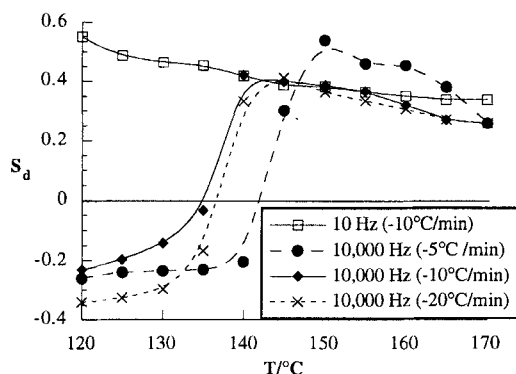


Figure 8. Effect of cooling on alignment of the material.

homeotropic to planar orientation occurred. Slower cooling rates ($-5^{\circ}\text{C min}^{-1}$) caused the transition to occur 10° higher than faster cooling rates.

During the isothermal transition from homeotropic to planar alignment, the small-angle diffraction pattern observed with the image intensifier became much more complicated. To investigate this microstructural change, WAXS patterns of the sample were obtained as a function of time after the material was cooled to 120°C at 10 Hz and the frequency increased to 10 000 Hz at time = 0. Figure 9 shows representative diffraction patterns as a function of time as the realignment occurred. The initial two equatorial wide-angle reflections at 0° and 180° split into 4 reflections which migrate azimuthally until they merge into 2 reflections at 90° and 270° , orthogonal to the original two reflections as shown in figure 10(a). The orientation parameter decreases as indicated by the weakening and broadening of these reflections. A well-defined split of each of the two wide-angle reflections occurs around 1 min and recombination occurs around 3.5 min. Once recombined, the orientation parameter (director orthogonal to the original direction) increases as indicated by the increase in the intensity of the two wide-angle reflections at initial times. The splitting into four reflections is thought to be caused by the rotation of the director in two directions azimuthally opposite each other as shown schematically in figure 10(b). The complexity of the small-angle region, due to the complicated initial diffraction pattern shown in figure 9,

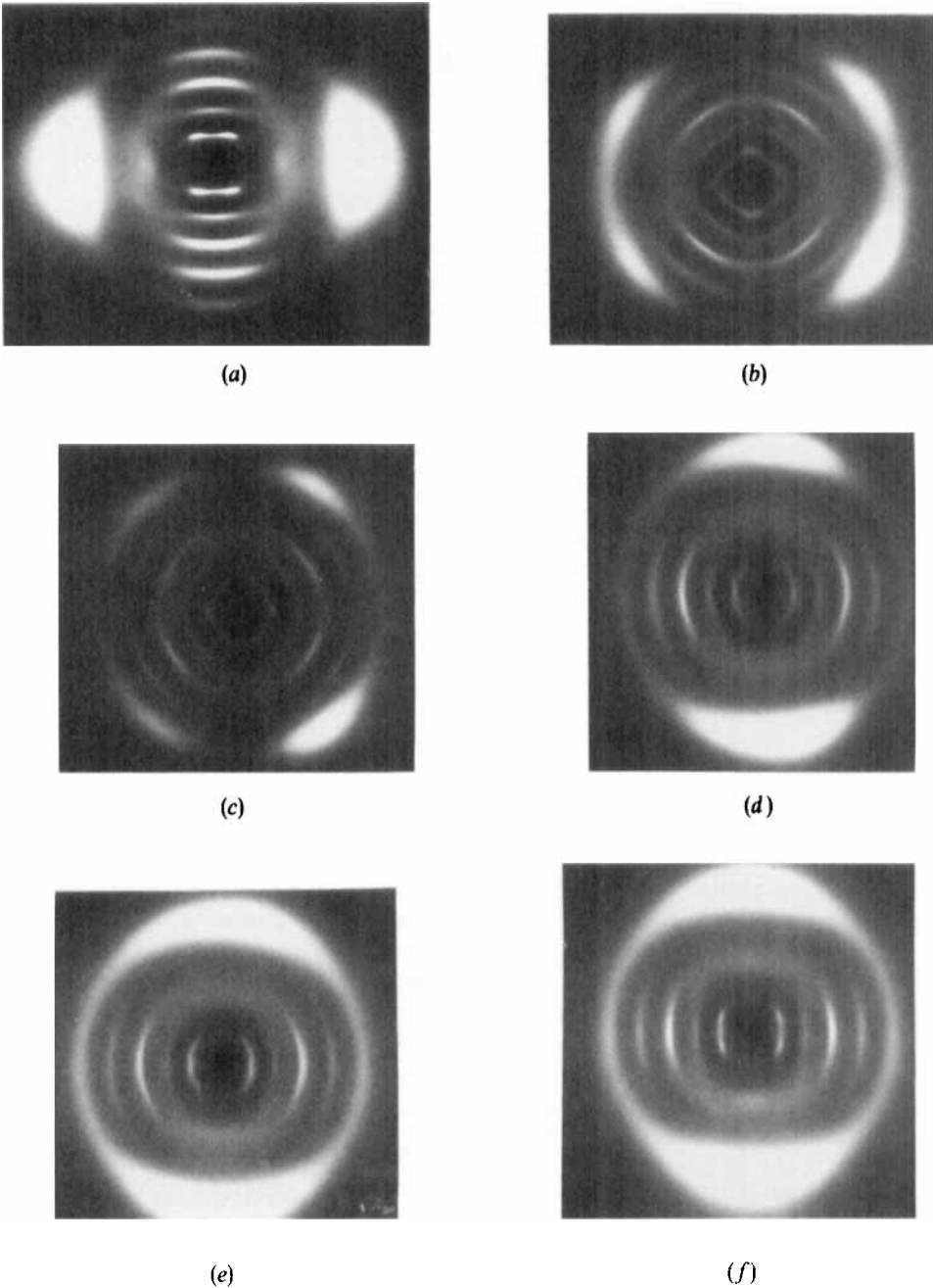


Figure 9. WAXS photographs as a function of time during reorientation from homeotropic alignment to planar alignment. Note the splitting at the intermediate times. (a) $t=0$, (b) $t=60$ s, (c) $t=105$ s, (d) $t=180$ s, (e) $t=210$ s, and (f) $t=300$ s. E -field direction is vertical.

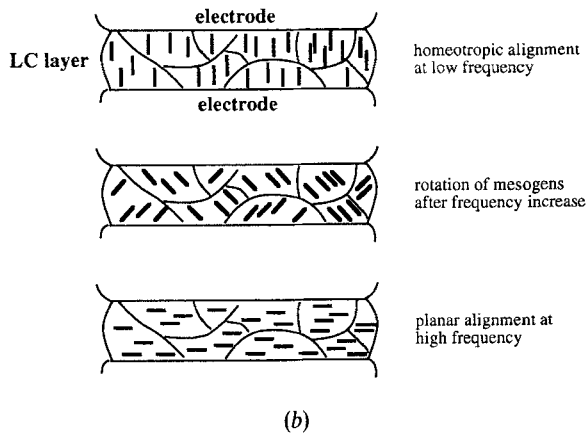
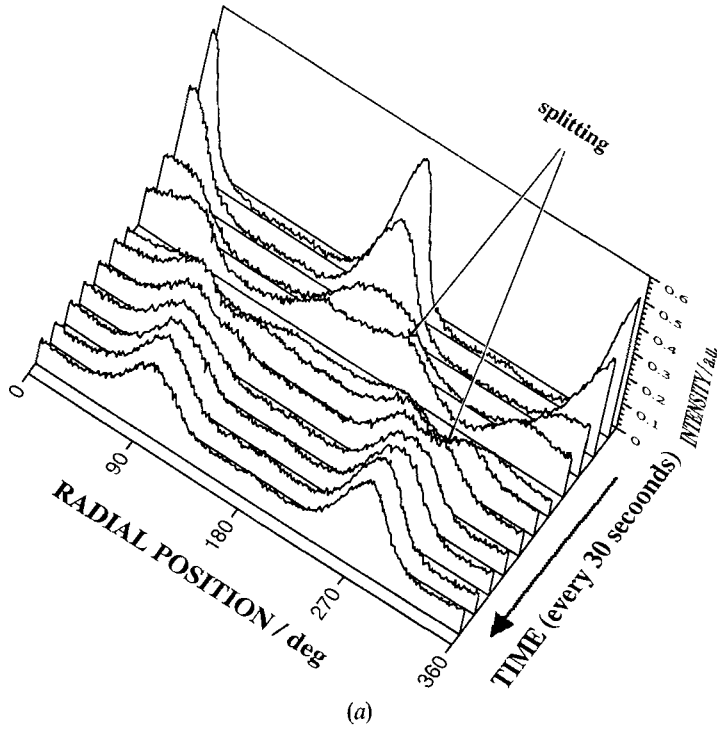


Figure 10. Reorientation of the wide-angle reflections as a function of time when frequency is switched (a) and schematic representation of the cooperative domain rotation during the frequency-mediated reorientation (b).

will be discussed in a forthcoming paper. After switching, the complexity of the X-ray pattern has been greatly reduced as revealed by the disappearance of the initial 4-spot pattern and the broader equatorial reflections.

4. Conclusions

The high flux of synchrotron radiation allows the monitoring of response of oligomeric liquid crystalline materials to an applied electric field in real-time. This technique is clearly a powerful tool for quickly and efficiently mapping the microstructural response of liquid crystalline systems to applied fields, provided the response times of the order of seconds to minutes.

Orientation parameters were typical for a nematic system and exhibited the expected trends with temperature. The response times varied from less than a second to a few minutes depending on temperature. At the low temperature limit of the mesophase, increased viscosity resulted in longer response times and a reduction in the orientation parameter. Careful attention to the thermal history of the sample during the alignment process allows one to tailor the orientation of the system. Two types of orientation were observed depending on frequency and temperature. The realignment from homeotropic to planar alignment was monitored. Also observed as a function of time was the splitting of the equatorial wide-angle reflections followed by their rotation into meridional positions. Substantial differences in the diffraction patterns between the planar and homeotropic orientations indicate differences in the influence of the electric field on the molecular arrangement of the mesogens.

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