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Alignment of a Smectic Side Chain Liquid Crystalline Polymer Using Surfaces and Alternating Electric Fields

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Alternating electric fields can align the smectic A side chain liquid crystalline polymer poly(MO6ONS) while it cools from the isotropic phase to the smectic phase, forming an optically transparent texture. The effect occurs only above a threshold electric field strength, and depends strongly on sample thickness and cooling rate, and weakly on electric field frequency. The aligned monodomain is stable up to the smectic-isotropic transition temperature (although there is some pretransitional light scattering close to the transition), and is homeotropic, optically uniaxial, and shows strong meridional x-ray diffraction peaks due to the smectic layers.

Surface fields can also align this material, producing similar monodomains, but only with samples below a certain thickness. It seems that this thickness is independent of the cooling rate.

Keywords: side chain, liquid crystalline polymer, smectic, alignment, electric field, surface

INTRODUCTION

Side chain liquid crystalline polymers, designed for applications such as photonic circuits and intelligent mirrors, are the subject of much research.[1,2,3] The possible device properties of the mesogenic groups (e.g., field alignment, NLO effects, piezoelectricity) are enhanced by the backbone, which can lend mechanical strength, promote optically clear glassy phases, and enhance the liquid crystalline properties by coupling. It also opens up the route to multifunctionality by preventing segregation of different units chosen for their specific activities. The mesogenic groups are attached to the backbone through a flexible spacer, which itself has a significant influence on the phases formed.[4]

In the production of devices, a thorough understanding of the effects of external fields on the material is essential. The self-alignment of liquid crystals in their nematic or smectic phases may be influenced by surfaces, electric and magnetic fields, stress, and flow history. Much research has already concentrated on electric and magnetic field effects,[5,6,7,8] particularly with the aim of increasing the NLO properties of the material,[9,10] and smectic A polysiloxanes have been aligned using alternating electric fields.[11]

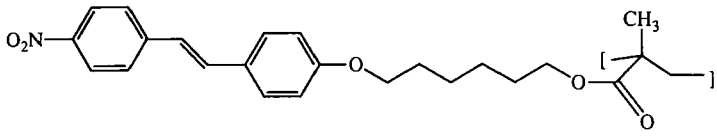

FIGURE 1 Poly(MO6ONS).

In a miniaturised device, surface fields will be more important than in a bulk sample. Small angle neutron scattering studies of some smectic side chain liquid crystalline polymers aligned in a magnetic field show that the backbone has an oblate anisotropy and is strongly confined to the layer planes.[12] These observations give us clues as to how the mesogenic groups are likely to behave if the backbone is aligned, or how the backbone will behave if the mesogens are anchored by a surface.

The material studied here is one of a range[13] synthesised at Hoechst-Celanese in Summit, New Jersey, USA, is referred to as poly(MO6ONS) and its structure is shown in Fig. 1. Great care was taken to ensure high purity and high resistivity, and poling fields of strong d.c. were sustainable without breakdown.

EXPERIMENTAL PROCEDURE

Sample Preparation

The homopolymer is melt-pressed between glass slides which are partially coated with indium tin oxide (ITO) as follows.[14] Partially oxidized ITO coated glass[15] is masked with nail varnish, etched with acid, rinsed in water, and the nail varnish washed off using acetone. The glass is then thoroughly cleaned in a Soxhlet extractor using propan-2-ol.

The glass is put in a cold vacuum oven with powdered polymer on the ITO strip, pumped down to vacuum, and heated until the polymer forms the isotropic phase. Air is admitted before cooling, so that any voids collapse.

The glass is put on a hot-stage with another identical piece of glass on top, heated up, and pressed so that the polymer spreads without trapping any air. The sample is now viewed in sodium light so that interference fringes are visible, pressed with tweezers until only a few fringes are seen, and cooled. The edges of the sample are sealed with epoxy resin, and the sample is reheated to relieve stresses. Finally, 50 μm steel or aluminium wires are stuck to the exposed ITO strip with conducting paint.

The thickness of the sample is measured just beside the polymer using a visible-UV spectrophotometer. Scanning from, say, 600 nm to 800 nm produces interference fringes, allowing the sample thickness d to be calculated from the wavelength

at one fringe λ_1 and the wavelength λ_2 at another one Δm fringes away (the refractive index is 1 because the gap is in air).

$$d = \frac{\Delta m}{2\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)}$$

Light Scattering Setup

On cooling from the isotropic phase, a highly scattering texture usually forms at the smectic-isotropic transition ('clearing point'). However, when a strong alternating electric field is applied across the sample while it is cooled, a clear texture forms.

The sample is placed in a nitrogen atmosphere in a Linkam THM600 hot-stage on a transmitted tungsten light microscope with all the polarisers removed, and a clean area of the sample is selected. Light intensity, and hence clarity, is measured with a photoresistor and care is taken to avoid photobleaching of the sample.

During the experiments, the sample is heated to about 10°C above the clearing point, the electric field is switched on, and the sample is then cooled at a controlled rate to about 10°C below the clearing point where it is held while readings are taken, and the electric field switched off.

LIGHT SCATTERING RESULTS

While the sample is cooling, the amount of light transmitted is reduced, as a scattering texture, which is characteristic of the polydomain smectic, forms. The

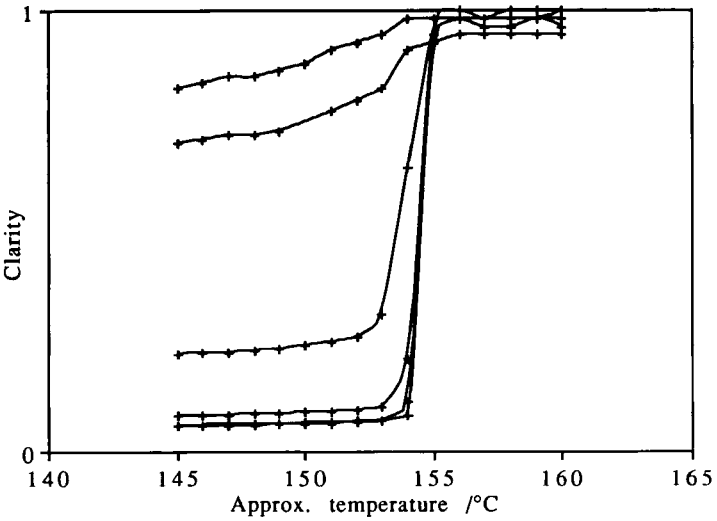

FIGURE 2 Clarity of sample while cooling at 2°C/min in 1 kHz peak–peak sinusoidal electric fields, showing an increase in scattering as the temperature falls. Peak–peak voltages are (from bottom) 0, 20, 40, 60, 80, 100 V.

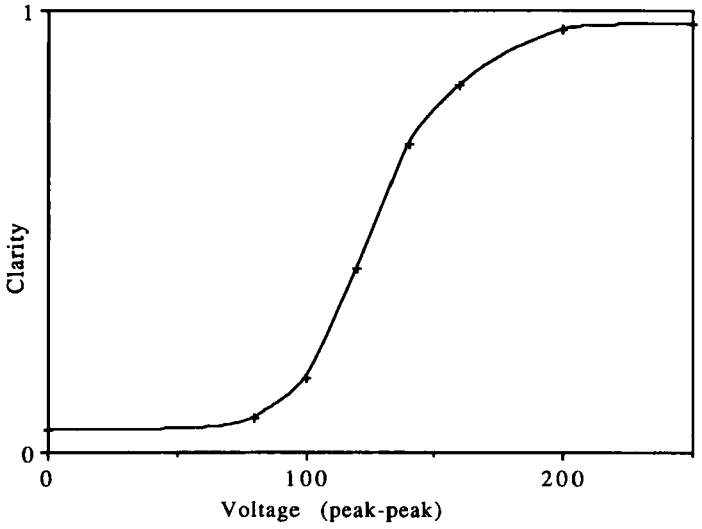

FIGURE 3 Clarity after cooling a 30 μm thick sample at 10°C/min in 3.33 kHz sinusoidal electric fields.

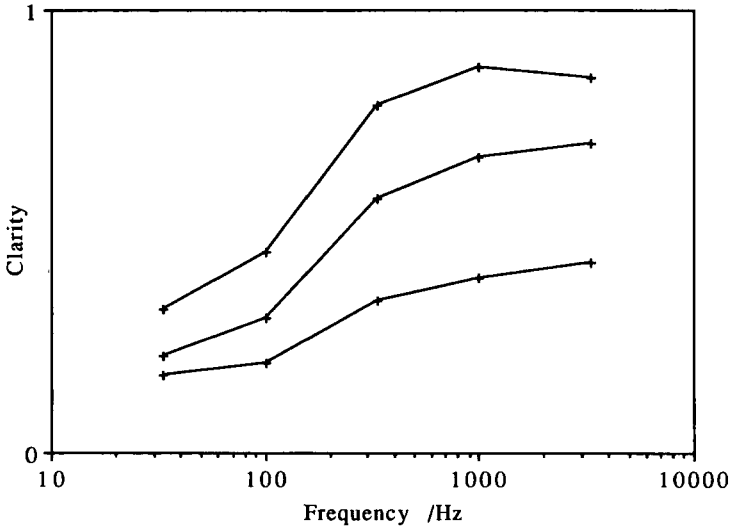

FIGURE 4 Clarity of a 30 μm thick sample after cooling in electric fields of various frequencies. Peak–peak voltages are (from top) 160, 140, 120 V.

amount of scattering depends on the strength of the electric field applied, as shown in Figs. 2 and 3.

The clarity is poorer after cooling in lower frequency fields (in the range studied) as seen in Fig. 4. Although it is a fairly weak effect, this has previously been reported[17] for small molecule smectic A devices aligned at constant temperature; at high frequencies, dielectric alignment occurs, and at low frequencies, electro-hydrodynamic instabilities cause scattering. However, in polymers these take time

to develop, so in our case the poorer clarity may be due to poor alignment, because the side groups can oscillate at the lower frequencies.

As might be expected, there is a linear relationship between the sample thickness and the voltage which just clears the sample (this is defined by taking tangents to the straight parts of the clarity-voltage curve, and taking the onset voltage to be midway between the voltages where these lines intersect the tangent to the steepest part of the curve). However, the line does not pass through the origin, but intersects the thickness axis at 11 μm, implying that a sample of this thickness would form a clear, homeotropic texture without the aid of an electric field. More interestingly, the intersection is at 11 μm no matter what the cooling rate is; one might expect it to be greater for slower cooling. These results are summarised in Fig. 5.

In Fig. 6 the gradient of the voltage-thickness lines are plotted against the log of the cooling rate, giving a good straight line fit.

This allows us to relate these variables empirically:

$$V = (2.65 + 3.38 \log_{10} c)(d - 11)$$

where V is the peak-peak voltage at which the sample just clears, c is the cooling rate in °C/min, and d is the sample thickness in μm.

We tried to align the material by holding it below the clearing point with an alternating voltage across it (40 μm thick, 400 V pk–pk, 3.33 kHz), but the sample was no clearer after 2 hours, despite using a voltage more than double that needed to clear the sample during cooling from the isotropic phase.

A sample which had been cleared using a strong electric field was reheated to about 10°C below the clearing point, and held to see whether the scattering texture returned. After 100 hours it was, if anything, clearer after cooling than before the

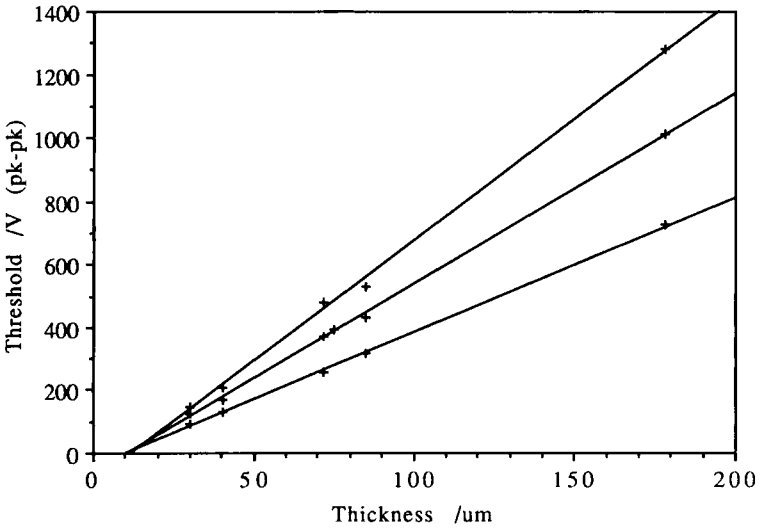

FIGURE 5 Pk–pk voltage (3.33 kHz) at which the sample just clears, plotted against the sample thickness for three different cooling rates (from top, 30, 10, 3°C/min).

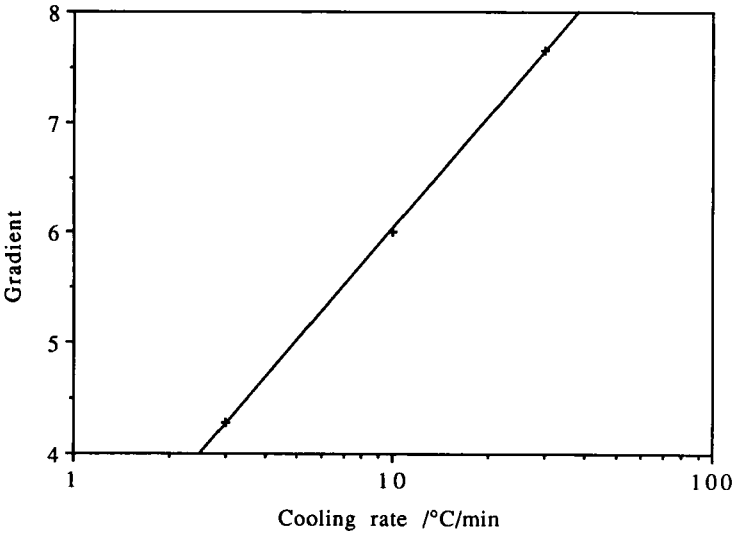

FIGURE 6 Gradient of lines from Figure 5 against cooling rate.

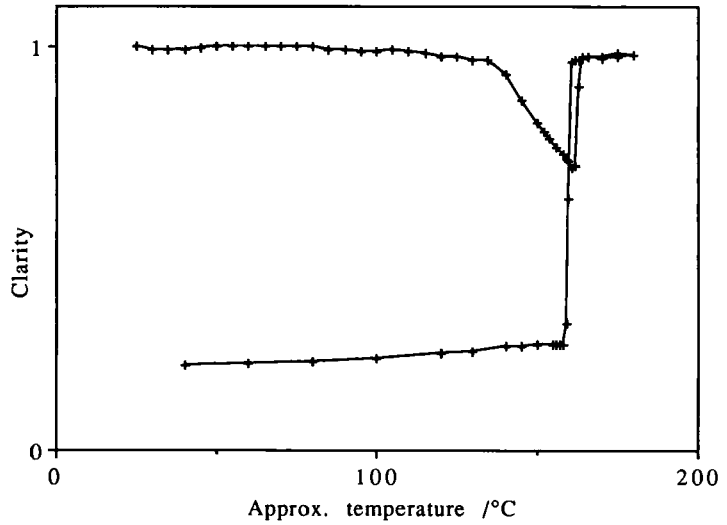

FIGURE 7 Reversible light scattering in a highly aligned, annealed sample, reheating (top line) at 5°C/min with no electric field applied, and permanent scattering on cooling again (bottom line).

anneal. It was then reheated to above the clearing point, with its clarity being continuously monitored (see Fig. 7).

As it approached the clearing point, pretransitional light scattering was seen, but the scattering disappeared if it was recooled (the same phenomenon is also seen in unannealed samples). This is thought to be due to local loss of order caused by statistical fluctuations, although it may also indicate the presence of a biphasic region. The molecular weight of the polymer is high ($\overline{M}_w \approx 990{,}000$), but its polydispersity ($\overline{M}_w/\overline{M}_n \approx 4.1$) would allow a biphasic region to form.[16] This would

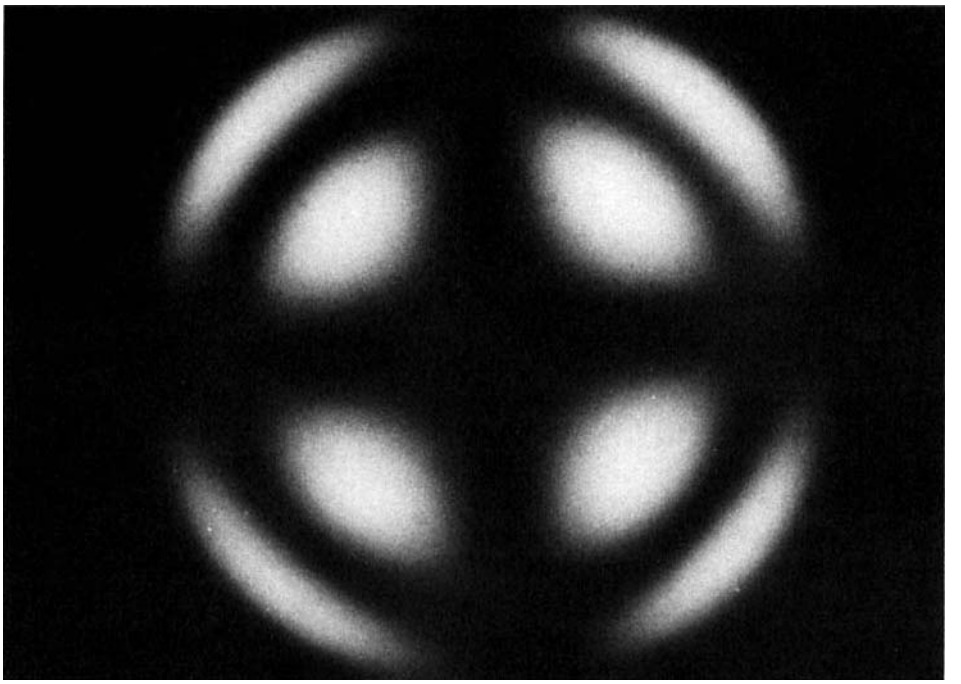

FIGURE 8 Conoscopic image, looking normal to the film in sodium light, of an electric field oriented film.

explain the absence of pretransitional alignment, and provide a mechanism for the observed effects. However, if the temperature rose above the clearing point, then the permanent scattering texture normally found in this material returned. What is remarkable is the way in which the clear, aligned texture survives a long heat treatment at about 150°C; this is an advantage in device manufacture.

MICROSTRUCTURE OF THE CLEAR TEXTURE

Conoscopy† shows that the clear texture is a uniaxial, homeotropic monodomain (see Fig. 8). It has a maximum birefringence of about 0.1, measured by standing the sample on its edge on a microscope stage, looking through it (between crossed polars held at 45° to the vertical) at a sodium light, and measuring the angle between the zero order and first order extinction, using the graduations on the microscope stage; this effectively measures the position of the first ring on the conoscopic image.

Microbeam x-ray diffraction patterns were taken from a single flake of aligned material (see Fig. 9). The interchain peaks (the large bright lobes) are restricted

† The reader unfamiliar with conoscopy is referred to Chapter 10 of *An Introduction to Crystal Optics* by Peter Gay (Longman, pbk reissued 1986) ISBN 0-582-30112-2.

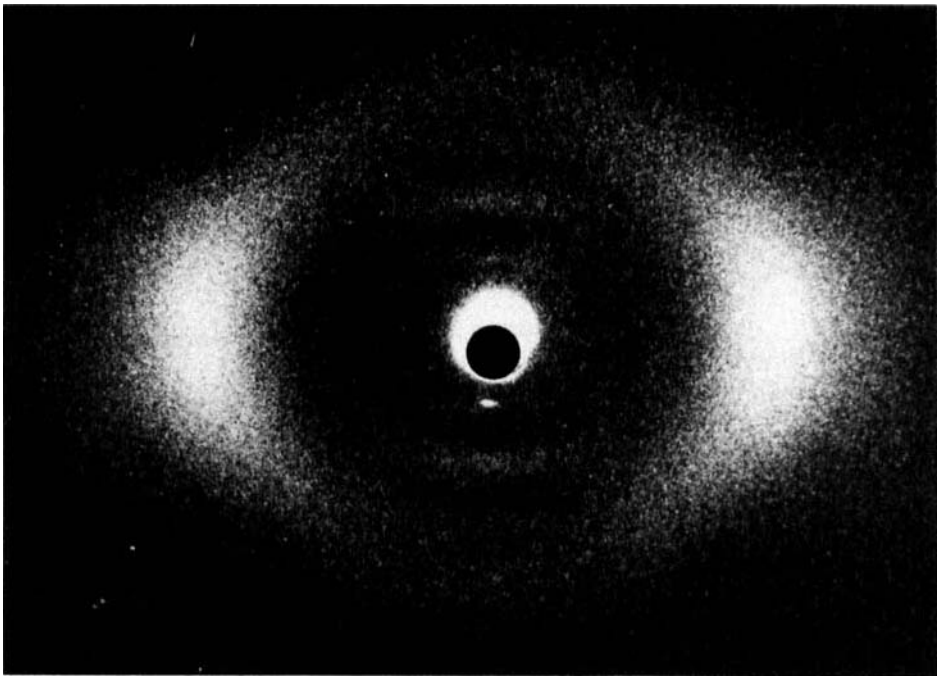

FIGURE 9 X-ray diffraction pattern using microcollimated monochromatic CuKα radiation incident in the plane of a small fragment of electric field aligned film. (Plane of film horizontal.)

to a narrow range of angles instead of forming a full halo; this indicates good alignment of the side groups. The smectic layer peaks are visible on the meridion.

A Philips vertical reflection diffractometer was also used, and a tungsten baffle was placed above the sample to reduce the air scattering from the main beam and allow scanning to lower angles (see Fig. 10). The two sharp peaks are due to smectic layers 33 Å apart, which is consistent with a fully interdigitated smectic A structure with the layers lying normal to the electric field, and parallel to the glass surfaces.

A 6.3 μm thick sample prepared at Hoechst-Celanese, by spin-coating onto ITO coated glass and baking for 16 hours to drive off solvent, also showed a uniaxial, homeotropic conoscopic image, and smectic layer peaks were visible in amongst the interference pattern caused by the ITO coating (see Fig. 11). This confirms that ITO coated glass can align this material in the absence of an electric field, so long as the sample is thin enough. Our melt-pressed samples, all of which are thicker than about 30 μm, failed to show such alignment even after annealing for 100 hours a few °C below the clearing point.

CONCLUSIONS

Alternating electric fields, stronger than about 5 V μm^{-1}, can produce highly oriented transparent textures in poly(MO6ONS) while cooling from the isotropic phase. The voltage required to produce alignment is strongly dependent on the

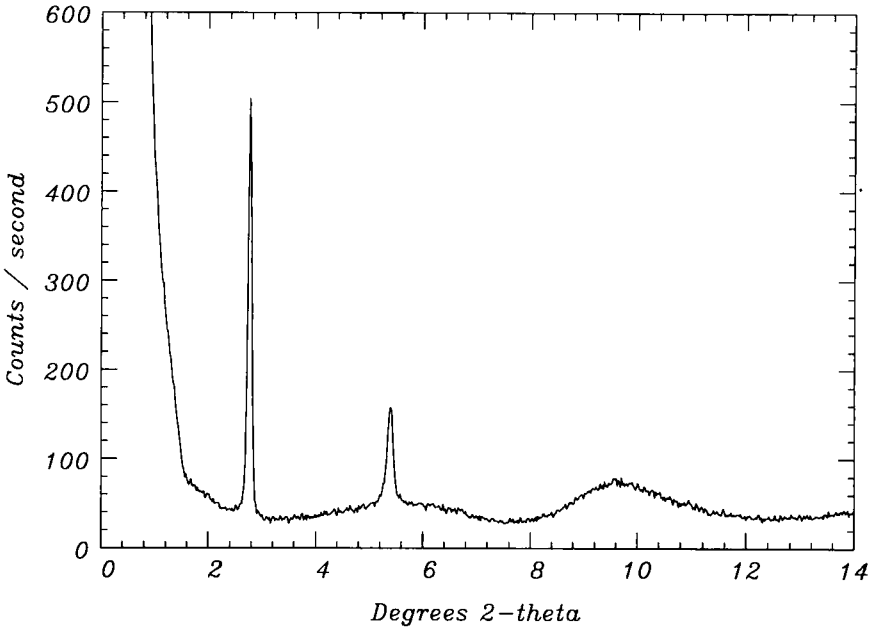

FIGURE 10 Meridional scan using monochromatic CuKα radiation from a film aligned by an electric field.

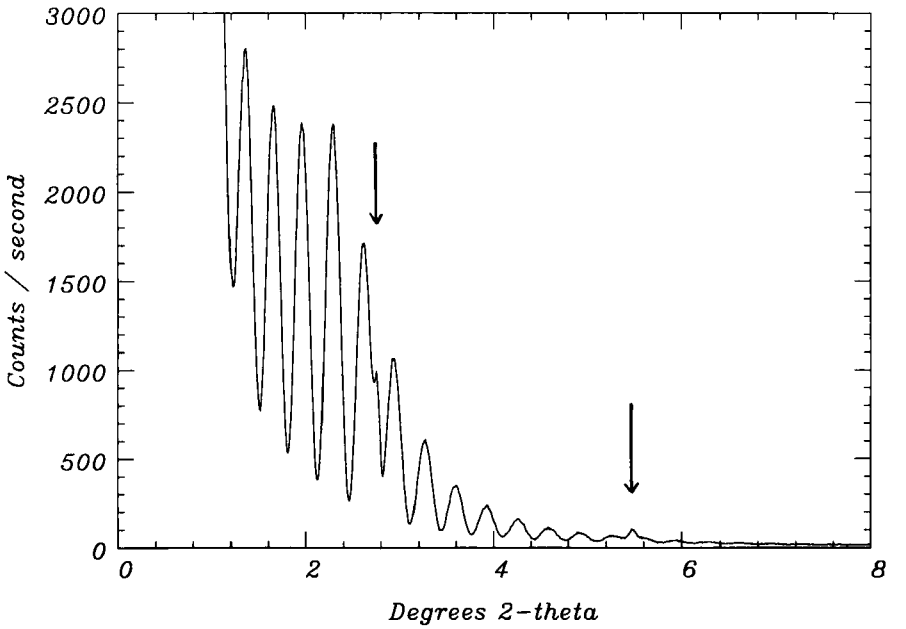

FIGURE 11 Meridional scan from a surface aligned film on an ITO coated glass substrate.

sample thickness (straight line relationship not through the origin) and on the cooling rate (logarithmic law). The resulting smectic A monodomain is stable at all temperatures below the clearing point (156°C), and has a layer spacing of 33 Å. It is predicted that thin samples ($\lesssim$11 μm) will be aligned by the ITO coated glass substrate alone, but this has not been investigated; it is, however, found that thin spin-coated samples are aligned by the surfaces on annealing.

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