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Smectic liquid crystal alignment using mechanically rubbed *n*-octadecylsiloxane self-assembled monolayers

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In recent years a variety of techniques has appeared for the fabrication and manipulation of self-assembled monolayers (SAMs). This development now offers new tools for the study and control at the molecular level of the interaction of liquid crystals (LCs) with solid surfaces, a research area of great importance for liquid crystal applications. In this paper we show that mechanically rubbed octadecylsiloxane SAMs generate a novel surface alignment of LCs in which the in-plane surface anisotropy usually accompanying rubbing is operative, but only for smectics in which the mean molecular long axis, $\hat{n}$, is tilted from the layer normal. On our SAMs smectic phases align with the layers parallel to the SAM surface, and in tilted smectics the surface component of $\hat{n}$ is along the rubbing direction. This anisotropy is absent in the nematic phases which align with $\hat{n}$ strictly normal to the surface. This behaviour can be understood in terms of a rubbed SAM monolayer surface, which is low energy, molecularly smooth, and rendered anisotropic by the rubbing. UV irradiation of rubbed SAMs gave excellent planar alignment ($\hat{n}$ parallel to the surface). This type of control over LC alignment has not been previously reported.

1. Introduction

Liquid crystal (LC) alignment, the control of the macroscopic domain structure of molecular orientation, is typically achieved by interaction of the LC with specially treated solid surfaces [1]. Alignment technology is the key to successful application of LCs, but current commercial alignment systems, formed from rubbed 20–100 nm thick crystalline polymer films, are of complex morphology, only poorly understood, and not optimal in many respects. This is especially true for ferroelectric liquid crystals (FLCs), since with these chiral, layered and tilted LC phases, alignment is much more subtle and complex than for conventional nematic LCs, and many applications benefit from unusually thin alignment layers.

Alkane-based self-assembled monolayers (SAMs), in particular octadecylsiloxane SAMs on oxidized silica surfaces, are aliphatic monolayers having a very low surface free energy and large H_2O contact angle ~110° [2]. These properties are a result of the tight packing of aliphatic chains of the SAMs, and the molecularly smooth surface, and distinguish SAMs from other silane and siloxane-based surface treatments that have been used to align LCs [1]. As part of a project aimed at exploring FLC alignment on novel surfaces, we have examined the alignment characteristics of Sagiv-type alkylsiloxane SAMs [2, 3]. Initial results of this study, which demonstrate a unique and potentially useful alignment approach, are presented herein [4].

2. Results and discussion

2.1. *Preparation of rubbed SAM substrates*

SAMs on float glass microscope slides were prepared using a procedure developed in these laboratories [5, 6]. A toluene solution of fresh octadecyltriethoxysilane (2% by weight) and *n*-butylamine catalyst (0.5% by volume) was prepared in a staining jar. Up to five float glass microscope slides were then immersed in this solution for 90 min. The slides were then removed from the solution, rinsed with fresh toluene, and cleaned by wiping the surfaces in one direction with a Kim Wipe (this initial rubbing sets the 'rubbing direction' of the substrates for subsequent steps). The substrates were then allowed to sit at room temperature for at least 24 h before further manipulation. While 'rubbing' is sometimes explicitly avoided in the SAM literature [7], in

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the context of LC alignment it takes on key importance, as described below. In our hands this type of mechanical cleaning after deposition improves the quality and consistency of the monolayers, and is common in the SAM synthesis literature [8].

2.2. *Cell fabrication*

LC alignment experiments with the octadecylsiloxane-coated float glass slides were performed as follows. A single SAM-coated slide was cleaned by rinsing with acetone or hexane, and rubbed in the same direction half a dozen times with a Kim Wipe at high 'finger' pressure. The slide was then cut in half along the short axis of the slide, and the two resulting substrates were used for LC alignment experiments. One such substrate was placed on a temperature-controlled surface, and the second substrate was placed upon the first, oriented such that the rubbing directions were either parallel or antiparallel. The plates were placed such that a non-overlapped area on the bottom plate could serve as an LC filling 'launch pad,' and the pair of plates was heated above the isotropic transition temperature of the LC to be used to fill the cell. No spacers were used to create these cells. A drop of LC was then placed on this surface close to the top plate, and the sandwich was allowed to fill by capillary action with the LC in the isotropic phase, as shown in figure 1 for the parallel-rubbed case. The LC layer in cells fabricated in this manner was ~10–15 μm thick (this estimate is based upon the observed birefringence colours in planar-aligned cells for various LC materials).

2.3. *Alignment of an achiral I-N-A-C material on mechanically rubbed SAM-coated substrates*

Initial experiments were performed with the achiral smectic LC material ZLI3234B (E. Merck, Darmstadt with phase sequence: Cr↔SmC←76→SmA←80→N←96→I). Cells prepared as described above were observed by transmission polarized light microscopy using a standard hot stage/microscope set-up. Excellent extinction was obtained for all sample orientations, indicating homeotropic alignment of the nematic phase, in which the director is normal to the surface. Such homeotropic alignment was seen upon cooling from the isotropic liquid, and for the entire nematic LC temperature range. Indeed, in the polarized light microscope the nematic phase was indistinguishable from the isotropic phase, though the transition was readily apparent by direct observation of the cell. However, upon heating, an alignment transition could be seen as indicated by a brief flash of transmitted light just before the transition to the isotropic liquid.

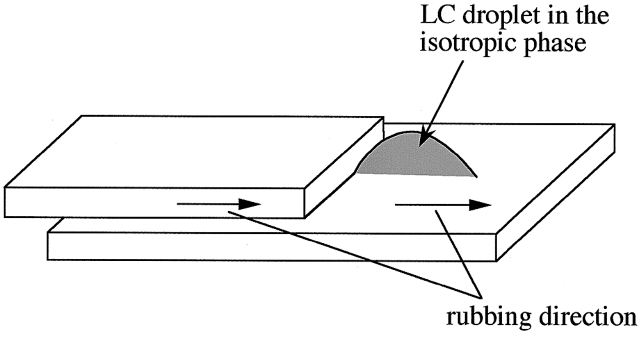

Figure 1. The technique used to fabricate the cells described herein. In this case the bounding plates are oriented such that the rubbing directions are parallel. The bottom plate rests on a hot plate such that the temperature of the sample is above its clearing temperature.

Excellent homeotropic alignment was also observed in the smectic A phase, i.e. the smectic layers align parallel to the plates. Thus neither the nematic nor smectic A phase alignment shows any visible effect of the rubbing. By contrast, upon entering the smectic C phase, wherein the layering remains parallel to the plates, but the molecular director must tilt to have a projection onto the layer plane in some direction (given by the unit vector $\hat{c}$), a clear indication that the rubbing direction was influencing the alignment was observed. Two different textures were obtained depending upon whether the substrates were oriented parallel or antiparallel. With antiparallel substrates a uniform alignment of $\hat{c}$ is found (a Schlieren monodomain). The anisotropy of the azimuthal orientation of $\hat{c}$ produces in-plane optical anisotropy which is easily seen upon sample rotation. The unidirectional rubbing of the SAM is found to align the $\hat{c}$ director parallel (or antiparallel) to the rubbing direction. With this orientation on each plate, and with antiparallel rubbing on the two substrates, a uniform $\hat{c}$ field is produced.

Rotation of the cell such that the polarizer is parallel to the rubbing directions (with the analyser oriented at 90° to the polarizer) gave a uniform dark state, as illustrated in figure 2A, while rotation of the cell by 45° afforded a uniform bright state. When the bounding plates were oriented with their rubbing directions parallel, however, a bright texture showing many defects was observed, as shown in figure 2B.

2.4. *Alignment of a chiral I-N*-A*-C* ferroelectric liquid crystal*

Similar experiments were carried out with the commercial chiral FLC mixture SCE9 (Merck Ltd, UK, phase sequence: Cr↔SmI*←< −20→SmC*←61→SmA*←91→N*←115→I). In this case, using either parallel or antiparallel-oriented bounding plates, on cooling, the expected homeotropic N* and A* textures (with no detectable birefringence in the plane) were followed by a very dark uniform homeotropic C* texture

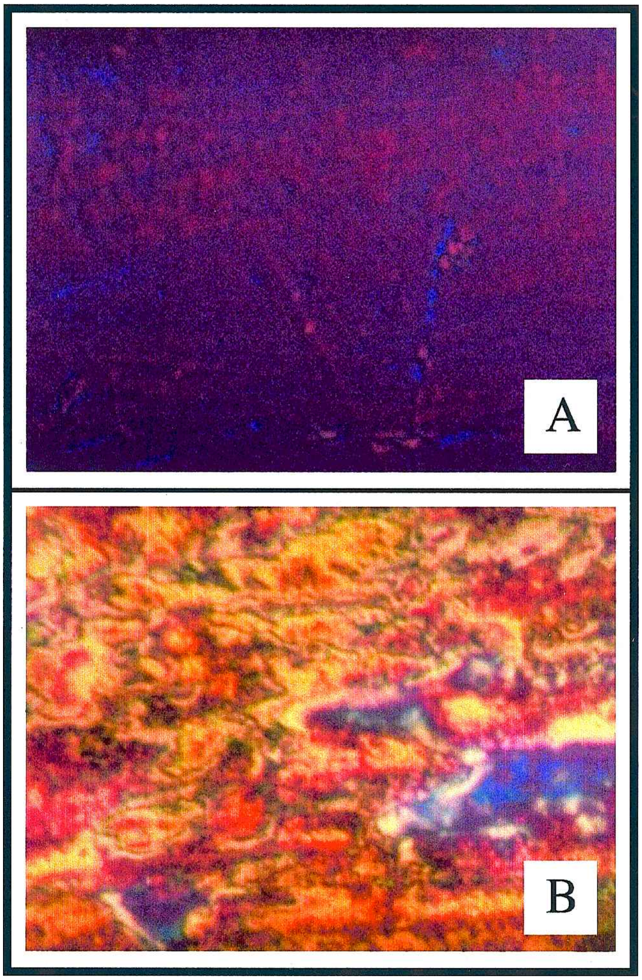

Figure 2. Polarized light photomicrograph showing the textures observed in the smectic C phase of the achiral mesogen ZLI3234B between rubbed SAM-coated float glass plates (a first order filter was used to bring out contrast in the textures). (A) Uniform texture observed between antiparallel-rubbed plates; (B) defect texture observed between parallel-rubbed plates.

showing no birefringence between crossed polarizers. In particular, the defect-filled texture observed in the cell filled with achiral smectic C with parallel-rubbed substrates was not observed with the chiral smectic C*.

2.5. *Interpretation of the alignment results*

Our interpretation of these observations is as follows. Typically when a homeotropic-orienting surface is rubbed, a tilt of $\hat{n}$ away from being strictly normal to the surface is found. We repeated such experiments using typical homeotropic alignment surfaces ('silanized' glass or glass coated with a thin film of lecithin [1]), which also gave a birefringent homeotropic C phase after rubbing (albeit with more defects than the SAM). However, they also invariably showed observable birefringence in the plane of the substrates in the nematic phase due to 'pre-tilt' in the homeotropic nematic [9]. It is also important to note that rubbing physisorbed monolayer surfaces gives undesirable effects due to non-uniform removal of the material [10].

To our knowledge, a surface treatment affording a non-birefringent homeotropic nematic with a uniform birefringent homeotropic smectic C phase has not been previously reported, and can be understood in terms of known properties of the SAM, as shown in figure 3 for the antiparallel-rubbed case. X-ray reflectivity from octadecylsiloxane SAMs on polished silicon wafers shows that the SAM surface is molecularly smooth, its interface with air being only ~2.5 Å thick and, that the alkane layer is packed at liquid hydrocarbon density [11]. This structure leads to the principal identifying characteristics of alkane SAMs: their low surface energy and low wettability. These features combine strongly to enforce homeotropic alignment of liquid crystal at the SAM surface by a mechanism similar to that operative at the liquid crystal–air interface in freely suspended smectic liquid crystal films [12]. Indeed, octadecylsiloxane SAM-coated plates identical to those described here have been used as solid substrates onto which freely suspended smectic LC films have been transferred [13].

At the LC–air interface layer, ordering parallel to the surface minimizes the surface tension, as evidenced by the quantization of film thickness in layer step units [12] and by X-ray reflectivity [14]. Even in bulk nematic samples free surfaces induced smectic-like layer ordering which penetrates into the bulk, typically a few layers at temperatures near T_{NI}, and diverging as T_{AN} is approached. We propose that the smoothness and low wettability of the SAM surface leads to free-surface-like behaviour of the liquid crystal, with the dominant surface effect being a tendency for the liquid crystal to layer order at the SAM surface, in all three phases. In the nematic and smectic A, the surface-induced layer ordering is smectic A-like and enforces a layer-normal director. The absence of anisotropy after rubbing indicates that the effect of rubbing is confined to the SAM itself and does not couple to the bulk nematic beyond the surface layer-ordered region. In the smectic C phase, on the other hand, an infinite susceptibility for tilt develops within the surface layers themselves, and the LC–SAM interaction establishes the azimuthal orientation.

Under these surface constraints, when the cells are antiparallel-rubbed, then the *c*-director is oriented in the same direction at both substrates, leading to a uniform Schlieren monodomain, as indicated in figure 3. Note that the data do not allow one to distinguish between the cases where the director tilts toward or away from the rubbing direction. Either case would afford a Schlieren monodomain with antiparallel-rubbed substrates.

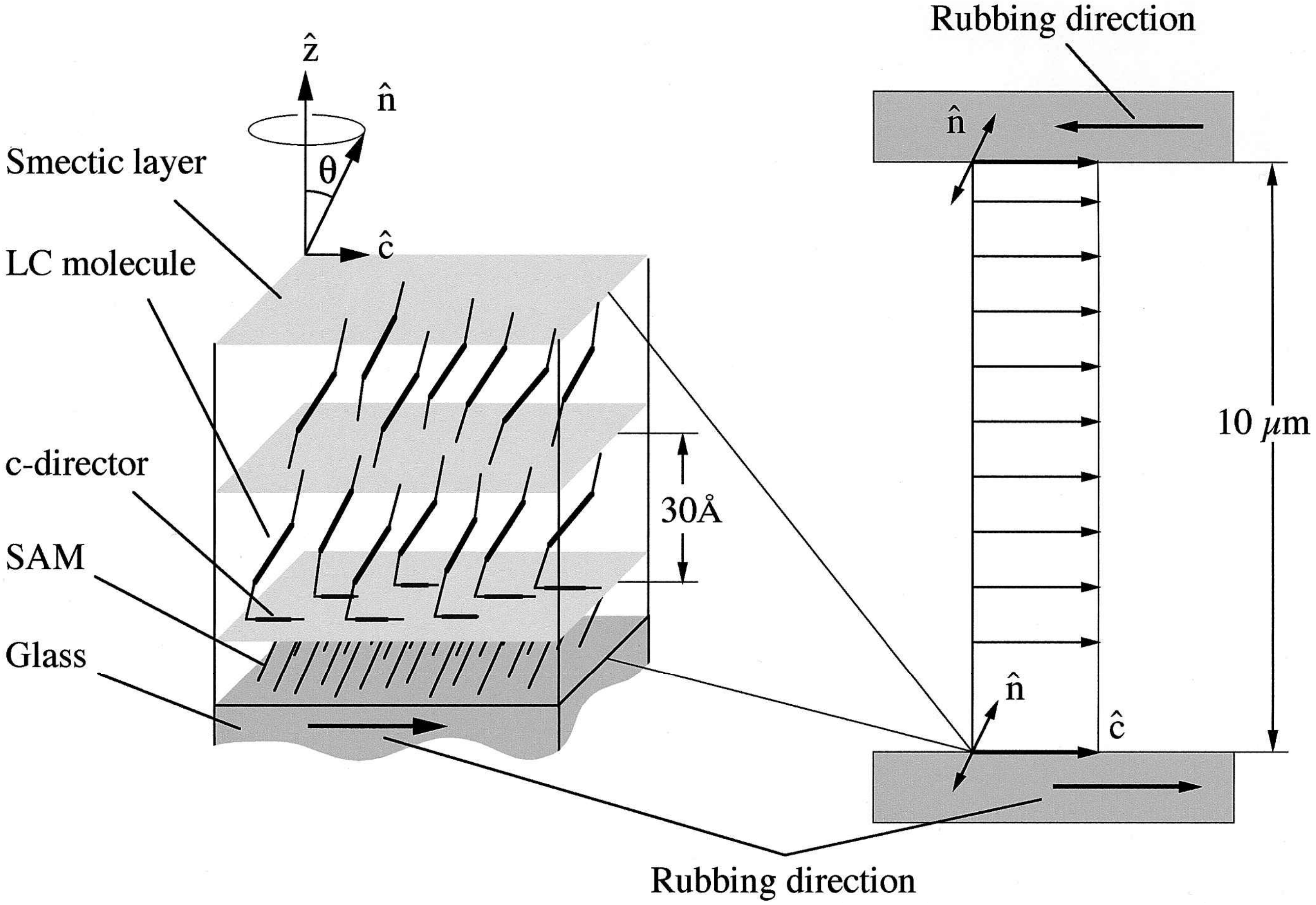

Figure 3. Illustration of the Schlieren monodomain structure observed with an achiral smectic C for antiparallel-oriented bounding plates. On the left is shown a detail of the surface and first two smectic layers. The layer normal ($\hat{z}$), C phase tilt angle (θ), director ($\hat{n}$) and c-director ($\hat{c}$) are all indicated on the drawing.

If, however, the bounding plates are oriented parallel, then the director must precess about the tilt cone by 180° (and the *c* director must rotate 180° in the plane parallel to the surfaces) on passing from one surface to the other, affording a helical structure similar to that observed in chiral C* materials, as illustrated in figure 4. For an achiral liquid crystal this twist is achieved only at some elastic free energy cost, driven by azimuthal anchoring of the *c*-director at the surfaces.

In an achiral or racemic mesogen, the helix may equally likely be left-handed or right-handed. It is reasonable to suggest that both right-handed and left-handed domains indeed form, with some defect structure mediating the boundary between such domains, as indicated in figure 4. Since the helix pitch is long and the birefringence in the plane is very small, lack of good extinction (a relatively bright texture at all orientations of the cell) is to be expected. The presence of both signs of the helix, with domain walls mediating the change, accounts for the defect-filled nature of the texture. If the director were free to take up an orientation either parallel or antiparallel to the rubbing direction, then the indicated twist would not be required, and a uniform director structure similar to that indicated in figure 3 would be expected for parallel-rubbed cells.

The results obtained with the chiral FLC material SCE9 are quite consistent with this analysis. If the helix pitch in the smectic C* phase is short relative to the thickness of the cell, then several turns of the helix will be present in a homeotropic Schlieren monodomain†. If the tilt at the bounding plates is opposed, then an odd number of half-twists of the helix should occur, as illustrated in figure 5A for 3/2 turns of the helix. This structure is very similar to that obtained in the achiral case shown in figure 4, *but with the same handedness*

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†The C* pitch of SCE9 at room temperature is 7 μm. This measurement was made by Dr. Michael Wand and Ms. Rohini Vohra of Displaytech, Inc. using a proprietary modification of the standard Cano wedge technique. The commercial supplier of SCE9 (Merck UK) does not report a value for the C* pitch of the material.

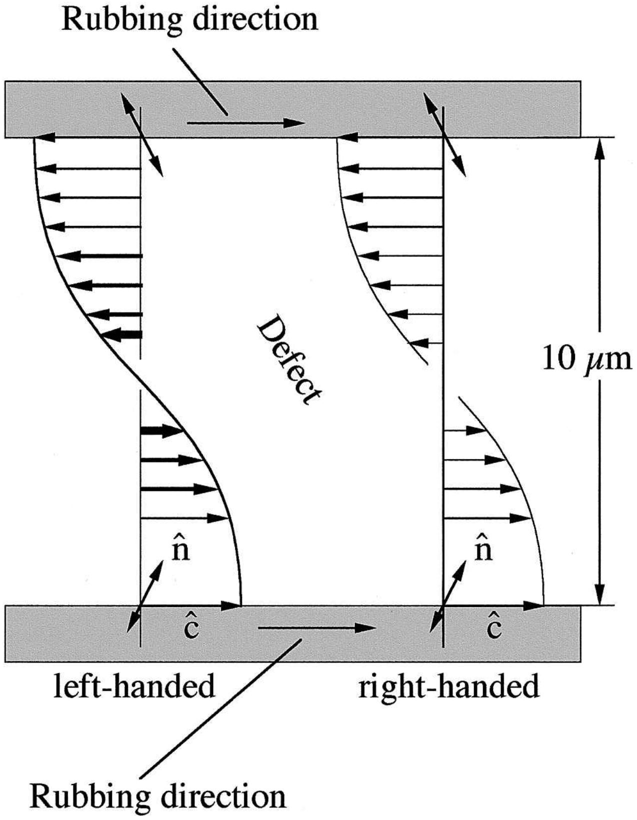

Figure 4. An illustration of the twisted director structure which occurs in the case of parallel-oriented bounding plates. When the LC is achiral, left-handed and right-handed twists have the same free energy, and should be equally likely, giving rise to defects.

throughout the entire sample. Thus, the defects observed in the achiral cell with parallel rubbing should not be present in the chiral case.

In addition, the small effective birefringence in the plane combined with a tighter pitch (compared with the achiral twisted cell illustrated in figure 3) averages the net *c*-director orientation, giving close to homeotropic optical behaviour, consistent with the dark, non-birefringent texture observed. The same argument applies in the case where the rubbing direction at the surfaces is antiparallel, as shown in figure 5B, except that an even number of half-twists of the helix is expected. The observed lack of birefringence in a uniformly dark texture would still be observed.

2.6. *Speculation on the mechanism of the azimuthal anchoring of the c-director*

While the results described above are consistent with a preferred director tilt either parallel or antiparallel to the rubbing direction at an LC/SAM interface, the interaction nevertheless appears polar (i.e. the *c*-director prefers to orient either parallel or antiparallel to the rubbing direction in a polar fashion). In an effort to probe further the origins of this apparently polar azimuthal anchoring at the surfaces in the smectic C and smectic C* phases, experiments aimed at determining the robustness of the polarity induced by the rubbing were carried out.

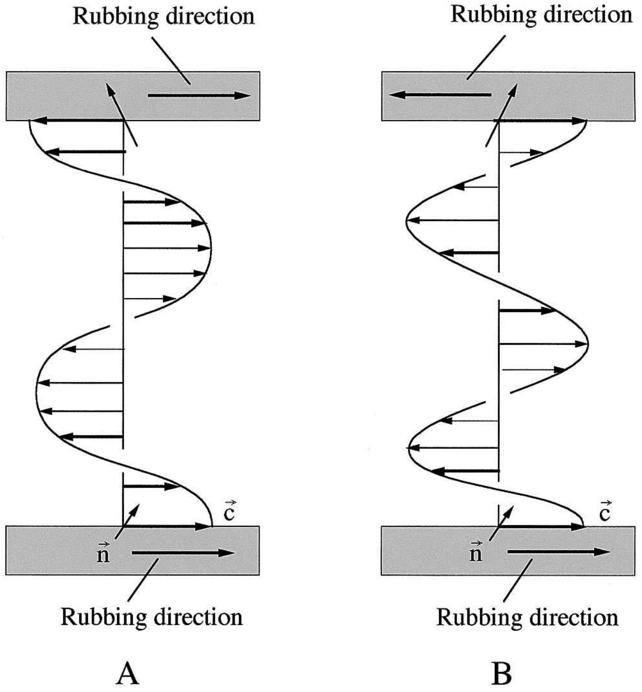

Figure 5. Uniform Schlieren monodomains expected for chiral C* mesogens with parallel or antiparallel-oriented bounding plates.

A cell fabricated as described above was dismantled, and the plates were rinsed with acetone. The plates were then scrubbed with a circular motion using a soft brush and detergent solution, and then rinsed with de-ionized water (the cells appeared completely dry after the rinse). Re-assembly of a new antiparallel-oriented cell using the achiral material ZLI3234B with these plates produced the same uniform tilt in the C phase as was initially observed when the plates were antiparallel. Sonication of the plates in detergent solution for 5 min, however, afforded plates giving a typical random Schlieren texture in the homeotropic smectic C phase upon re-fabrication of the cell. These results show that the polar behaviour observed for LC alignment on rubbed SAMs is a result of some feature of the SAM structure which is unaffected by simple washing with detergent, but is destroyed by sonication.

These results strongly suggest that the alignment observed on the mechanically rubbed SAMs results from the structure of the SAM itself, and not simply from ‘dirt’ on the surface of the substrates. One reasonable proposal is that the octadecyl chains in the SAM are tilted, and that mechanical rubbing orients tilted domains to provide a net tilt direction of the chains, as indicated schematically in figure 3. Such a net orientation of the tilt provides at least in principle a mechanism for the polar azimuthal anchoring of the *c*-director.

Results of LC alignment experiments with alkanethiol SAMs on obliquely deposited thin films of gold make an interesting comparison [15, 16]. Abbott *et al.* have shown that the nematic phase of 4-cyano-4′-*n*-pentylbiphenyl (5CB) aligns in a planar fashion (with the director parallel to the substrates) on SAMs composed of alkanethiols with chains of between 5 and 16 carbons. The gold film in these experiments was about 100 Å thick. Interestingly, when the alkanethiol chains were of odd carbon number, the nematic director oriented perpendicular to the direction of deposition of the gold, while the director was oriented parallel to the gold deposition direction for even carbon chain lengths. This beautifully subtle effect of SAM structure on LC alignment suggests that the orientation of the methyl group at the surface of the SAM controls the azimuthal anchoring interaction for the nematic phase of 5CB.

In the present case, homeotropic alignment is observed for all liquid crystals examined, including cyanobiphenyls. In the thiol/gold system, homeotropic anchoring of the nematic phase of 5CB could be obtained by inducing a rough surface topography using mixtures of thiols with different carbon chain lengths (C_{16} and C_{10}, with C_{16} predominant) [16]. While the siloxane SAMs on glass are neither as smooth nor structurally uniform as the heteroepitaxial thiol/gold system, we do not believe that the homeotropic anchoring reported here is caused by surface roughness. We propose, rather, that the polarizability of the gold film causes the change in zenithal anchoring from planar for SAMs on gold to homeotropic for SAMs on glass. That is, as discussed above, the octadecylsiloxane SAM on a glass surface behaves like the free surface with air in a freely suspended LC film. But, given the subtlety of the alignment results obtained with the thiol/gold SAMs, it is quite reasonable that creation of a net anisotropic tilt in the SAM, or even simply anisotropic orientation of the methyl groups at the surface, by mechanical rubbing, would provide for the polar azimuthal anchoring of the *c*-director as reported here.

2.7. *Photopatterning of the LC alignment*

It is known that UV-irradiation of a siloxane SAM on silicon modifies the monolayer such that the new surface is hydrophilic [17]. It is thought that the UV-exposure selectively breaks Si–C bonds in the SAM surface. The final result is a surface rich in SiOH groups, similar though not identical to the native glass. This observation suggested that it should be possible to pattern LC alignment by photolithography, since hydrophilic surfaces such as clean glass are known to favour planar alignment of LCs [1], while the hydrophobic SAM-coated surface favours homeotropic alignment. Recently, Clark and Lee realized this supposition by experimental demonstration of an approach to nematic LC alignment using photopatterned octadecylsiloxane SAMs on float glass [18]. In that case, the starting SAM-coated substrates were identical to those described here. Using simple lithographic masks, alternating stripes of exposed and unexposed regions were created. Though no anisotropy in the surface itself was generated, the wave vector of the stripes efficiently aligns the nematic phase of E31 (Merck UK) in domains with the director parallel to the plates and stripes. That is, while no part of the surface of these substrates possesses azimuthal anisotropy, the spatially patterned zenithal anchoring combined with the LC elastic constants serves to produce macroscopic LC alignment.

Here we report the behaviour of smectic LCs on photopatterned and mechanically rubbed octadecylsiloxane SAM-coated substrates. We find that both the unexposed SAM-coated regions and the UV-irradiated regions possess anisotropy in the plane as evidenced by azimuthal anchoring of the smectic LC *c*-director in the homeotropic regions as discussed above, and azimuthal anchoring of the molecular director in planar-aligned regions exposed to UV light.

SAM-coated plates were patterned with UV light using electron microscopy grids as shadow masks. The masked plates were irradiated for 0.5 h using a low pressure mercury lamp. After irradiation, just before fabrication of the cells, the plates were cleaned by rinsing with acetone and rubbing as before.

Cells were created as shown in figure 1, using a grid of square holes 30 μm along a side as the mask for patterning of the bottom substrate, and an unexposed antiparallel-oriented rubbed SAM-coated slide as the top substrate. When filled with ZLI3234B, the textures shown in figure 6 resulted. The photomicrograph of figure 6 labelled N1 shows the nematic phase of ZLI3234B close to the transition into the smectic A, between crossed polarizer and analyser, with the polarizer horizontal (in figures 6N1 and 6N2 the rubbing direction at the bottom plate is indicated by the white arrows, the distance between centres of the square areas of planar alignment is approximately 85 μm). The darkest region of figure 6N1 corresponds to the area where the light was prevented from reaching the surface by the mask, and is as expected homeotropic nematic. The slightly brighter areas in panel N1 correspond to areas where the bottom plate was exposed to UV-irradiation, and show a texture consistent with parallel alignment at the bottom plate and homeotropic alignment at the top plate (a ‘bent’ director

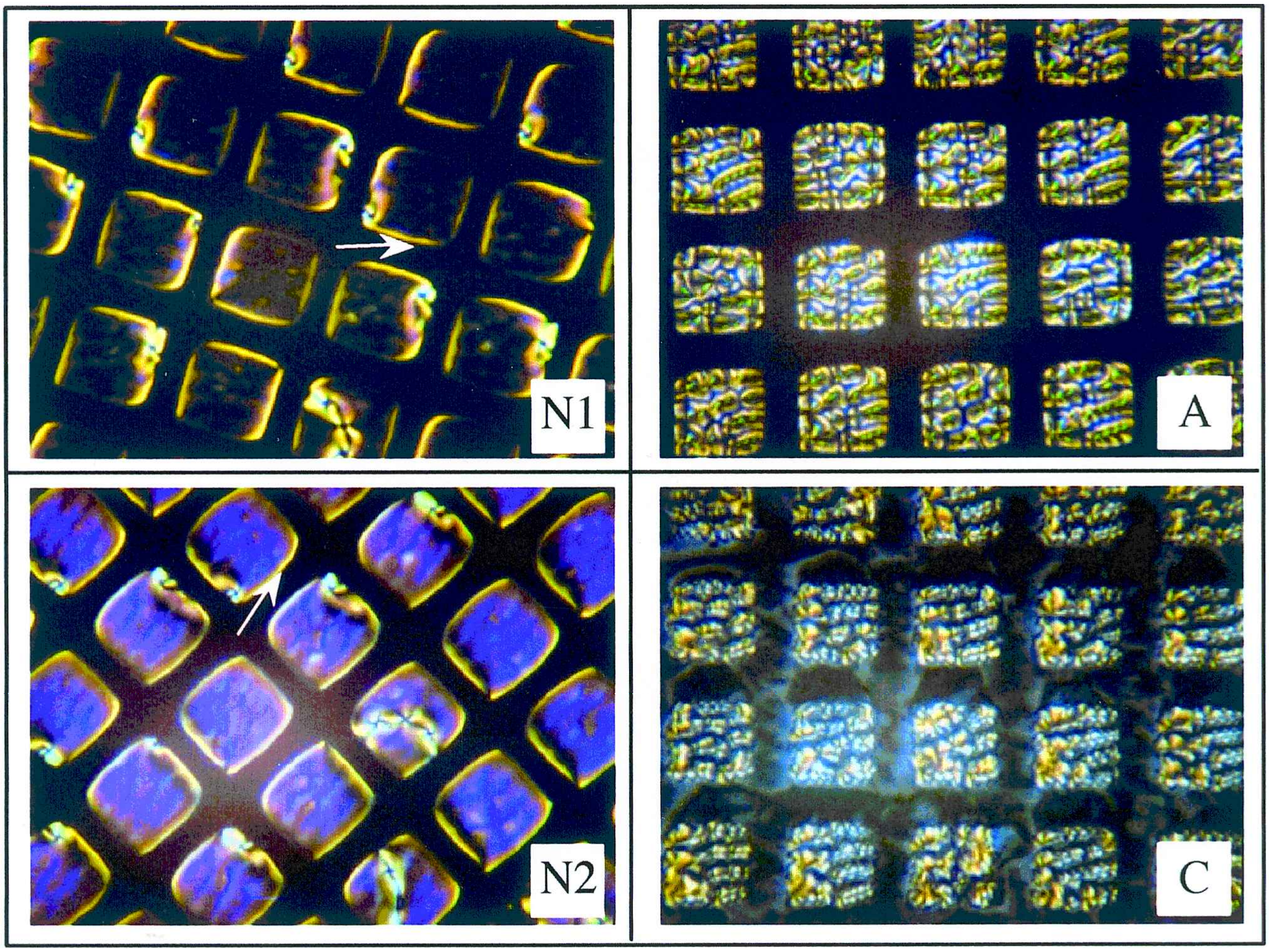

Figure 6. Photomicrograph of liquid crystal aligned on a UV-irradiated monolayer photopatterned with a 300 mesh grid shadow mask between crossed polarizers (horizontal and vertical). The cover slip has a monolayer which has not been photopatterned. The nematic phase is shown in figures 6N1, with the rubbing direction of the bottom plate indicated by the white arrow (the top plate is oriented with its rubbing direction antiparallel to that of the bottom plate). Figure 6N2 shows the same sample rotated by 45° such that the rubbing direction at the bottom plate is parallel to the polarizer. Figures 6A and 6C show the smectic A and smectic C phases, respectively, of the same sample.

structure). Rotation of the cell by 45° counterclockwise produced the image labelled N2. Note that the homeotropic regions stay dark, but the brightness of the 'bent' regions changes considerably when the cell is rotated due to birefringence in the plane caused by the bent director structure.

Panels A and C of figure 6 show the smectic A and smectic C phases, respectively, in the same cell. These images are also quite consistent with homeotropic alignment at both plates in the masked regions, and a complex texture of defects in the regions where the bottom plate favours planar alignment and the top plate favours homeotropic alignment.

Figure 7 illustrates the unique alignment possibilities achievable using SAMs with photopatterning. In this case, the shadow mask was an array of circular holes 300 μm in diameter. The top plate is patterned using orthogonal UV-irradiation through this mask to produce around 300 μm regions where the SAM has been exposed. The bottom plate in this cell was irradiated through the same type of mask, but with oblique irradiation such that the exposed regions were elliptical.

By manipulation of the filled cell, it proved relatively easy to overlap the irradiated areas on the top and bottom plates without the aid of a microscope. The photomicrographs were taken after the cell was reheated into the isotropic phase on the microscope hot stage, then cooled into the LC phases. Textures obtained in the nematic, smectic A, and smectic C phases are indicated. The aligning characteristics for both UV-exposed and unexposed rubbed SAMs can be seen in the figure. Consideration of the area labelled 'unexposed', an area where the two substrates are coated with antiparallel-rubbed SAMs, nicely illustrates the alignment of the

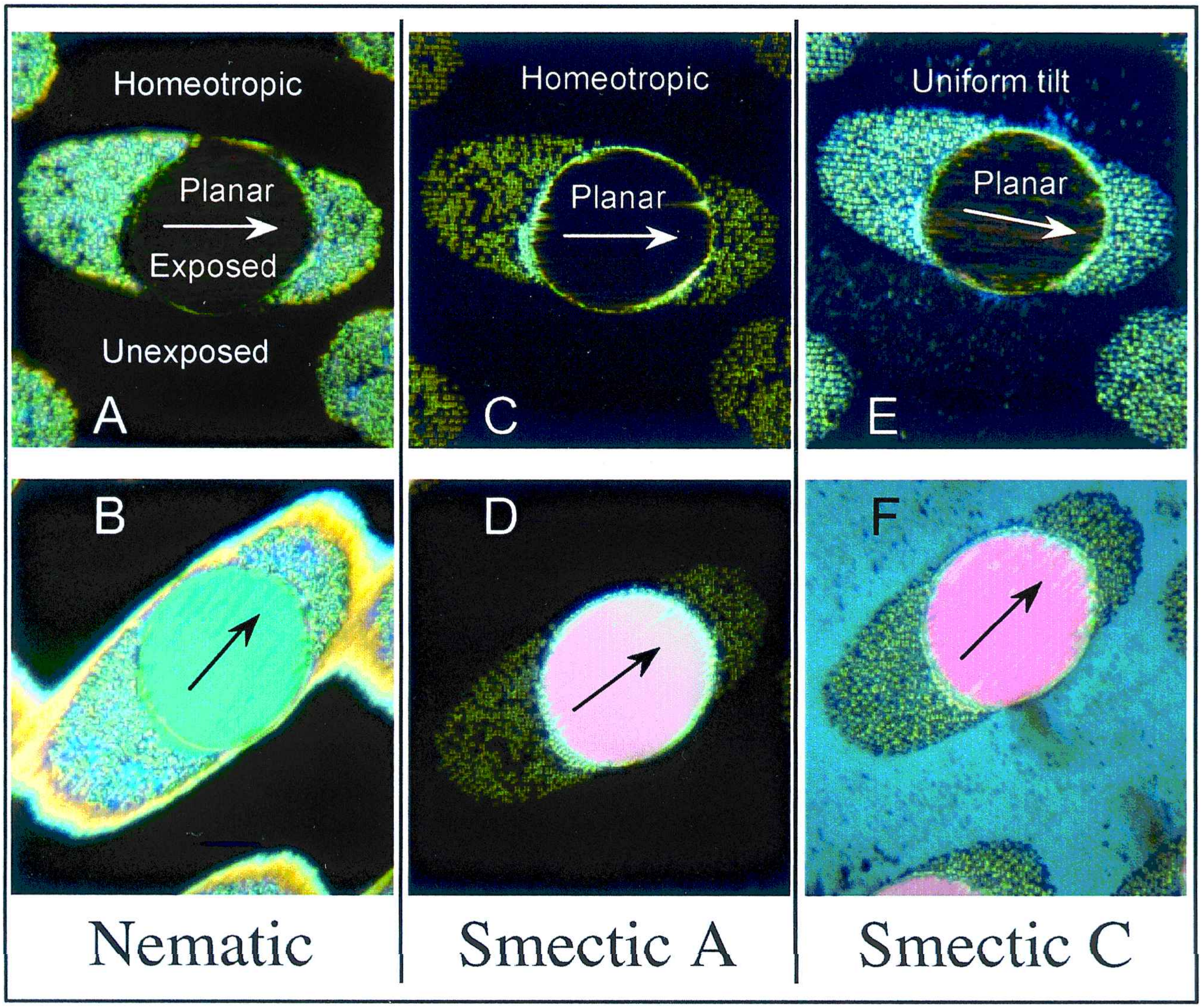

Figure 7. Photomicrograph of a liquid crystal on a UV-irradiated photopatterned surface as described in the text. The nematic, smectic A, and smectic C phases are shown with the rubbing direction (as indicated by the arrows) aligned with the crossed polarizers (top) and at 45° to the crossed polarizers (bottom).

three LC phases of ZLI3234B on unpatterned rubbed SAMs as discussed in detail above (homeotropic in the N and smectic A phases; Schlieren monodomain—labelled 'Uniform tilt'—in the smectic C phase). The polarizer and analyser were crossed, with the polarizer oriented horizontally. The arrows on the photographs in the panels A–F indicate the rubbing direction on the bottom plate. The grey birefringence colour at maximum transmission observed in the Schlieren monodomain (figure 7F) is a manifestation of the low birefringence in the plane resulting from the uniform orientation of the *c*-director.

Excellent alignment is also observed in the regions labelled 'Exposed,' where both plates have been irradiated and rubbed antiparallel. In this case the alignment is planar, with the molecular director more or less parallel to the substrates, and azimuthal anchoring consistent with the director orienting along the rubbing direction. As can be seen in figure 7A, the nematic phase shows good extinction when the polarizer is parallel to the rubbing direction. Rotation of the cell by 45° produced the texture shown in figure 7B; the homeotropic regions remain extinguishing, while the planar region shows transmission of light with a blue birefringence colour. In the smectic A phase, the planar texture in the exposed region also shows excellent azimuthal alignment, as indicated in figures 7C, D, with a pink birefringence colour.

While the birefringence of ZLI3234B is not published, the chiral material ZLI3654, likely composed mainly of similar components, was reported by E. Merck in their product documentation to have $\Delta n \sim 0.13$ in the smectic C* phase at 20°C. Assuming a similar birefringence in the smectic A phase of ZLI3234B, the pink colour in figure 7D may be assigned to the third order, suggesting an LC layer thickness of about 12 μm for this cell. This suggests that the blue birefringence colour observed for the nematic phase is second order, with $\Delta n \sim 0.10$.

Finally, the textures obtained from the smectic C phase shown in figure 7E, F illustrate the high degree of azimuthal anchoring of the *c*-director in the unexposed regions, and the good planar alignment, carrying over the smectic A phase, in the exposed regions. There is no apparent change in birefringence on transition from the smectic A to the smectic C phase, as expected for a 'non-de Vries' smectic A–C transition.

It is important to note here that the planar alignment observed for these cells in the exposed regions is considerably better than can be achieved by the rubbing of clean glass substrates, suggesting that after the irradiation, residual material is left on the surface which improves azimuthal anchoring. For substrates such as these, the azimuthal anchoring is maintained even after a methanol rinse of the substrates after the rubbing. The planar azimuthal anchoring, though not the homeotropic Schlieren monodomain, is lost on scrubbing the substrates with detergent, however†.

Finally, experiments involving shorter irradiation times were performed. At a threshold irradiation time of approximately 10 min, SAM-coated substrates begin by giving N phases birefringent in the plane but not planar-aligned. The smectic C phases on such plates show a Schlieren monodomain structure. Longer irradiation leads to larger birefringence in the N phase, until finally the plate gives parallel alignment, as described above in the 'long irradiation time' limit. These observations suggest that pretilted homeotropic nematic alignment can be obtained using photopatterned SAM-coated substrates, with the pre-tilt angle controlled to some extent by the irradiation time.

3. Conclusions

It has been demonstrated that octadecylsiloxane SAMs on float glass exhibit novel and interesting properties with respect to alignment of liquid crystals. Specifically, the data suggest that the achiral mesogenic mixture ZLI3234B using rubbed SAM-coated float glass plates gave homeotropic nematic alignment with no observable pretilt, a homeotropic smectic A phase, and a homeotropic smectic C phase wherein the director prefers to tilt either parallel or antiparallel to the rubbing direction, but not both. The chiral FLC material SCE9 exhibited very similar results, with homeotropic N* and A* alignment, and a helical Schlieren mondomain in the smectic C* phase. The polarity of the tilt direction apparently induced by the rubbing is quite robust, and azimuthal anchoring of the *c*-director is still observed after washing the plates with detergent.

Furthermore, UV-irradiation of the SAM on glass followed by rubbing produces a surface exhibiting planar alignment with azimuthal anchoring of the molecular director. This allows UV-lithographic patterning of homeotropic and parallel domains in LC films. When two patterned plates are aligned correctly, domains of smectic C phase exhibiting good planar alignment with the smectic layers normal to the rubbing direction, and good azimuthal alignment of the *c*-director in homeotropic domains, can be produced in the same sample.

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† This loss of memory of the rubbing direction in the hydrophilic areas of the plates such as those illustrated in figure 7 may be due simply to the fact that air-drying of the wet surfaces after cleaning with detergent leaves a residue which somehow masks the rubbing direction. This does not occur on the SAM-coated areas since they emerge dry from a water rinse.

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