Surface Memory Effects in Liquid Crystals: Influence of Surface Composition

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(Received 3 May 1985)

Certain polymer-coated solid surfaces prepared to produce an isotropic (random) planar liquid-crystal boundary condition can be rendered strongly anisotropic by exposure to orientationally ordered liquid-crystal phases. This effect reveals a plastic coupling of liquid-crystal molecular orientation to hydrophobic surfaces which is absent for hydrophilic surfaces.

PACS numbers: 61.30.Eb, 68.10.Cr, 81.60.Jw

Anisotropic solid surfaces such as obliquely evaporated SiO and rubbed polymer films are commonly used to control the molecular orientation in adjacent liquid-crystal (LC) phases.[1] In this Letter I present results of experiments which demonstrate and probe the complementary effect: initially isotropic (random planar) surfaces are rendered anisotropic by exposure to orientationally ordered LC phases. Since LC phases possess only weak translational order, making surfaces anisotropic in this way operates solely by virtue of the LC-surface orientational coupling. Hence this scheme represents a probe of LC-surface orientational interactions. The results show a plastically deformable coupling of a common thermotropic LC with hydrophobic polymer surfaces, which is absent for hydrophilic polymer surfaces; i.e., the latter are effectively slippery.

Such surface memory effects (SME) were first reported by Friedel,[2] who noted that the exposure of a clean, initially isotropic glass surface to contact with anisotropic crystals of compounds having rod-shaped molecules rendered the glass anisotropic. In particular, he found that exposed glass would orientationally order at the surface the molecular long axes of the nematic LC phase obtained by melting the crystals. I demonstrate here analogous liquid- and plastic-crystal surface memory effects, i.e., those obtained by exposure only to the liquid-crystal smectic-*A* phase and the plastic-crystal smectic-*G* phase.

Experiments were carried out with use of Pyrex-glass microscope slides,[3] coated by dip or spin methods with polymer layers ranging from a minimum thickness (obtained by dip coating followed by soaking and rinsing with the polymer solvent) up to about 1 μm in thickness. Coated slides were dried with the use of a jet of filtered nitrogen gas. Experiments were also carried out with the use of uncoated cleaned glass. The polymers and solvents used are noted below in Table I. The LC employed was heptyloxybenzylidene-propylaniline (7O.4), having the following phase sequence: [isotropic (*I*)] 74 °C [nematic (*N*)] 71.5 [smectic *A* (*SA*)] 64 [smectic *C* (*SC*)] 60 [smectic *G* (*SG*)]. The glass plates were assembled into cells without spaces so that the LC layers were typically 1 to 5 μm thick. The phenomena to be reported did not depend on the LC layer thickness in this range. With this LC all the surface treatments employed produced planar alignment.

The cells were filled by capillarity in the *I* phase and the surface preparations used produced the schlieren texture [Fig. 1(a)] upon cooling into the *N* phase. Repeated cycles of heating into the *I* and cooling into the *N* produced new schlieren textures with noyeaux in different places, indicating boundary conditions having the molecular director parallel to the surface, but with no average surface torque component normal to the surface. Such isotropic (random planar) alignment can be achieved either by having molecules free to rotate about the surface normal or by having the molecules fixed at the surface but with orientations that vary randomly over distances well below the microscope resolution.[4]

Figures 1(b)–1(e) illustrate typical *SA* and *SG* surface memory observations. These figures show the results of applying temperature sequences to cells with surfaces coated with polyvinyl alchohol (PVA) and polyimide (PI), starting with a virgin *N* sample, previously exposed only to the *I* phase and exhibiting a schlieren texture, lowering temperature into either the *SA* [Fig. 1(b) and 1(c)] or *SG* [Fig. 1(d) and 1(e)] phase, and reheating back into the *N* and/or *I* phase which are used as probes of surface anisotropy. Figures 1(b-i) and 1(c-i) show typical focal conic textures obtained upon cooling a planar 7O.4 sample 3 °C into the *SA* phase. The samples were left in the *SA* phase only long enough for the *SA* to cover the observation field (< 1 min). Returning to the *N* phase reveals a new schlieren texture for the PVA surface [Fig. 1(b-ii)], but a distinct departure from the schlieren texture for the PI surface [Fig. 1(c-ii)], the new texture reflecting in detail the local orientation adopted at the surface by the director in the focal conics of the *SA* phase. We refer to this stable anisotropization of the surface by exposure to an oriented phase as surface writing or as a surface memory effect.

Such surface anisotropization could be a homogeneous alteration of the surface or widely spaced anisotropic patches or pinning sites, as the latter can interact cooperatively to orient the nematic director.[4] Howev-

TABLE I. Surface memory effects observed with 7O.4 and Pyrex substrates coated with the indicated polymers.

Surface layer	Solvent	*SA* SME	*SG* SME	*SG*-induced reduction of γ_{SN}	Nematic wetting
PI[a]	Dimethyl-acetamide	strong	strong	yes	yes
Ny 6.6[b]	*m*-cresol	yes	yes	yes	yes
Ny 11[b]	*m*-cresol	yes	yes	yes	yes
Par[c]	Benzene	yes	yes	yes	no
Uncoated glass	· · ·	yes	yes	yes	no
PE[d]	Distilled water	no	no	no	no
PVA[e]	Distilled water	no	no	no	no
POE[f]	Distilled water	no	no	no	no

[a] SP510-polyimide resin, Toray.
[b] Nylons.
[c] Paraffin.
[d] SA73-polyester resin, American Liquid Crystal.
[e] SA72-polyvinylalcohol, American Liquid Crystal.
[f] Polyoxyethylene (molecular weight, 20 000).

er, bringing the sample into the isotropic phase demonstrates that the orientation is caused by local surface anisotropization. Figure 1(c-iii) shows the PI sample brought just into the *I* phase, 1.0 °C above the *N*-*I* transition temperature. Here the same orientation distribution as in the *SA* and *N* phases is evident in the thin, nematic pretransitional layers at the sample surfaces. This orientation of the nematic surface layers is induced by the now anisotropic surfaces, as is found for uniformly rubbed or evaporated anisotropic surfaces.[5] Because of the abrupt reorientations and patterns characteristic of the *SA* focal conic texture, the nematic surface layers in the *I* phase are readily oberved in a good polarized light microscope. The orientation of these layers by the surfaces indicates that anisotropy is imposed by the surface at points spaced by less than the nematic surface layer thickness (~ 100 Å). The *SA* SME is reversible—by rapidly cooling from the *N* into the *SA* phase, a new focal conic texture can be obtained which will reorient the surface to its texture.

Figures 1(d) and 1(e) show sequences obtained upon cooling into the *SG* phase and reheating. The *SG*, although generally included among the liquid-crystal layered smectic phases, is in fact a plastic crystal in which the molecules are tilted with respect to the layers but have disordered chains and are free to rotate about their long axes. The *SG* phase [Figs. 1(d-i) and 1(e-i)] is characterized by the usual mosaic texture of uniformly oriented domains corresponding to different orientations of the tilted director about the layer normal. Figure 1(d-ii) shows the same area returned to the *N* phase for a PVA surface. The schlieren texture indicates the absence of any permanent influence on the random PVA surface by exposure to the *SG*. Long exposure, up to 5 days, gives similar results. By contrast, Fig. 1(e-iii) shows the PI sample returned to the *I* phase, the nematic surface layers exhibiting orientation patterns identical to the *SG*. The intermediate *N* phase shows the same pattern, whereas it is not visible in the intermediate *SA* phase [Fig. 1(e-ii)] except very near the *SA*-*N* transition. The anisotropy imparted to the PI surface by the *SG* is much stronger than for the *SA* phase, since the *SG* previously written pattern overwrites any *SA* pattern and is unaffected by the subsequent presence of the *SA* phase.

Of particular interest with regard to the *SG* SME is its effect on the surface tensions of the solid (*S*)-*I* (γ_{SI}), *S*-*N* (γ_{SN}), and *N*-*I* (γ_{NI}) interfaces. The initial nematic schlieren texture appears as isolated circular drops on the solid surface when nucleating from the isotropic, indicating a finite contact angle of the *N*-*I* interface with the solid substrate. However, once the surface is written by the *SG*, the *N*-*I* contact angle is always smaller than before writing and for some surface treatments (Table I) the contact angle is reduced to zero and the nematic wets the solid substrate. This is the case for the *I*-phase sample of Fig. 1(e), in which the surface nematic layers have grown continuously out from the surface as the temperature was

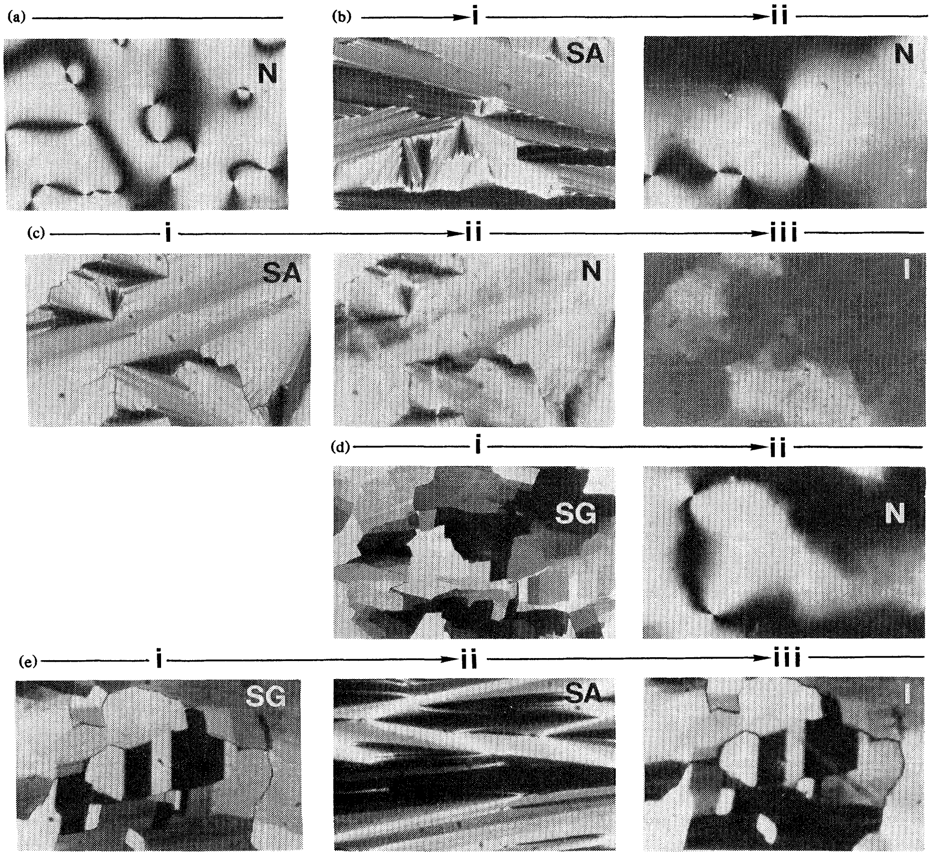

FIG. 1. Transmission photomicrographs between crossed polarizers obtained with use of a Lietz Orthoplan-Pol microscope. The field width of each picture is 400 μm. (a) Nematic (*N*) schlieren texture obtained upon cooling a virgin sample with polyethylene-glycol–coated plates from the isotropic (*I*) phase. This is typical of the schlieren textures obtained with virgin cells. (b) Smectic-*A* (*SA*) focal conic texture and *N* schlieren texture obtained by heating the *SA* PVA surfaces. There is no SME. (c) PI surface: (i) *SA* focal conic texture and (ii) *N* and (iii) *I* texture obtained upon heating. The similar orientation of the director at the surface into the focal conic pattern is apparent even in the *I* phase, indicating a local surface anisotropization by exposure to the *SA*. (d) PVA surface: (i) Smectic-*G* (*SG*) mosaic texture and (ii) *N* schlieren texture obtained upon heating. There is no SME. (e) PI surface: (i) *SG* mosaic texture and (ii) *SA* focal conic and (iii) *I* texture obtained upon heating. The *SG* pattern is not visible in the *SA* phase, but reappears in the *N* (not shown) and *I* phases. The nematic surface layers in the *I* phase grow continuously with decreasing temperature; i.e., this sample exhibits wetting by the *I* phase.

lowered toward the *N*-*I* transition. With employment of the arguments of Yokoyama, Kobayashi, and Kamei,[6] this wetting of the solid surface by the nematic is evidence that exposure of the surface to the *SG* phase induces, in the *I* phase, nematic order at the surface with a surface order parameter Q_s which is larger at the *N*-*I* transition than the nematic bulk value.

Hence exposure of a random polyimide-coated surface to the *SA* or *SG* phases alters the random planar surface condition to one which exhibits a surface anisotropy, which in the *SG* case is quite strong. By contrast, exposure of a random polyvinylalchohol-coated surface to the *SG* or *SA* produces no apparent surface writing: Melting to the nematic after exposure gives the random schlieren textures back again. This dependence on surface polymer coating led to experimentation with a variety of surface treatments, the results of which are shown in Table I. The surface treatments are listed in order of the strength of their surface memory effect, those exhibiting the strongest at the top. "Strength" was assayed qualitatively, on the basis of the existence of the *SA* SME, the *SG* SME, and surface wetting. The table shows a striking characteristic of the SME for polymer-coated surfaces: Hydrophilic (water soluble) polymer coatings, like PVA and poethylene glycol (PEG), exhibit no or only very weak SME; hydrophobic (organic soluble) polymer coatings, like nylon and PI, exhibit the strongest SME.

This distinction was enhanced as the thickness of the polymer coating increased. That is, the SME's became stronger with increasing surface layer thickness for the hydrophobic polymers and weaker for the hydrophilic. For clean glass weak to moderate SME's were observed, probably associated with the adsorption of LC layer or organic surface active contaminant on the glass surface.

Our interpretation of these observations is as follows. The *N-SA* transition in 7O.4 is first order, the *SA* nucleating in batonnets. As the *N-SA* interface spreads over the sample surface the nematic director at the surface is oriented locally normal to the layers into the focal conic geometry. We can estimate the surface torque required to cause rotation of the director through an angle θ from its preferred *SA* orientation as follows. This rotation requires an energy per unit area of $U=(KD)^{1/2}\theta^2$, where K is a Frank constant and D is the smectic orientational elastic constant.[7] For typical values of $K=10^{-6}$ erg/cm and $D=10^8$ ergs/cm^3, the surface energy (torque) density for $\theta=1$ rad is $\lesssim k_BT/(40\ \text{Å}^2)$. For the hydrophobic polymer surfaces exhibiting a strong SME there is a surface layer which is plastically deformable under this torque, and more so under the presumably stronger torque in the *SG* phase. As mentioned above, even for strongly *SG* written surfaces, the surface pattern disappears in the *SA* phase, indicating that the *SA* director adopts the *SA* focal conic orientation down to within a few tens of angstroms of the surface. This is expected since orientations caused by surface torque will penetrate only a distance $(K/D)^{1/2}\gtrsim 10$ Å into the *SA*. Near the *N-SA* transition D may decrease leading to larger ξ and the observed reoriented surface regimes or, alternatively, the *N-SA* transition temperatures may be raised by the orientational strain within ξ of the surfaces. This will be the subject of focus for study.

In the *SA* phase there are solely orientational elastic torques on the director field, since the translational ordering is very weak; that is, constraining the director at the surface plastically deforms it. The deformable surface in the hydrophobic case is likely a mixed polymer-LC layer, possible since materials like 7O.4 exhibit some solvent character. Partial miscibility could produce an interfacial region which is rigid but where the LC solvent softens the polymer, reducing its yield torque density below that applicable by the director in oriented smectic phases.

For the hydrophobic surfaces the absence of any SME for an initially random planar surface implies the absence of orientational coupling to the director field, i.e., that the surface is orientationally slippery. However, this behavior can come about in two rather distinct ways, which cannot be distinguished on the basis of the present or related experiments. On the one hand, there could be no orientational coupling between the director and the surface on any length scale; that is, individual molecules are free to reorient. Alternatively, the surface-LC coupling could be strong but elastic, the director at a random planar surface being forced into an orientation pattern which is macroscopically random but uniform on a submicroscopic correlation length scale, r. The macroscopic result would be azimuthal orientational degeneracy. Absence of an SME for the strong-coupling case would require this coupling to be elastic: Either the surface torques are too small to significantly influence the local orientation, or, since the LC and the polymer are immiscible, the polymer layer remains rigid, returning the LC director to its locally random orientation once the surface torques are removed. If r is smaller than the nematic correlation length in the *I* phase at the *N-I* transition, then these two cases cannot be distinguished in macroscopic experiments such as these reported here or studies of wetting. Finally, it should be noted that since the polymer films were not baked, they were likely to contain some solvent, particularly water for the hydrophilic polymers, which is likely to enhance further the hydrophilic-hydrophobic distinction.

The author acknowledges the support of this work by Centre National de la Recherche Scientifique and U.S. Army Research Office Grant No. DAAG29-83-K-0076, and the assistance of the Centre Recherche Paul Pascal liquid-crystal group.

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[1] J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures,* Molecular Crystals and Liquid Crystals, Suppl. 1 (Gordon and Breach, London, 1982).

[2] G. Friedel, Ann. Phys. (Paris) **18**, 273 (1922).

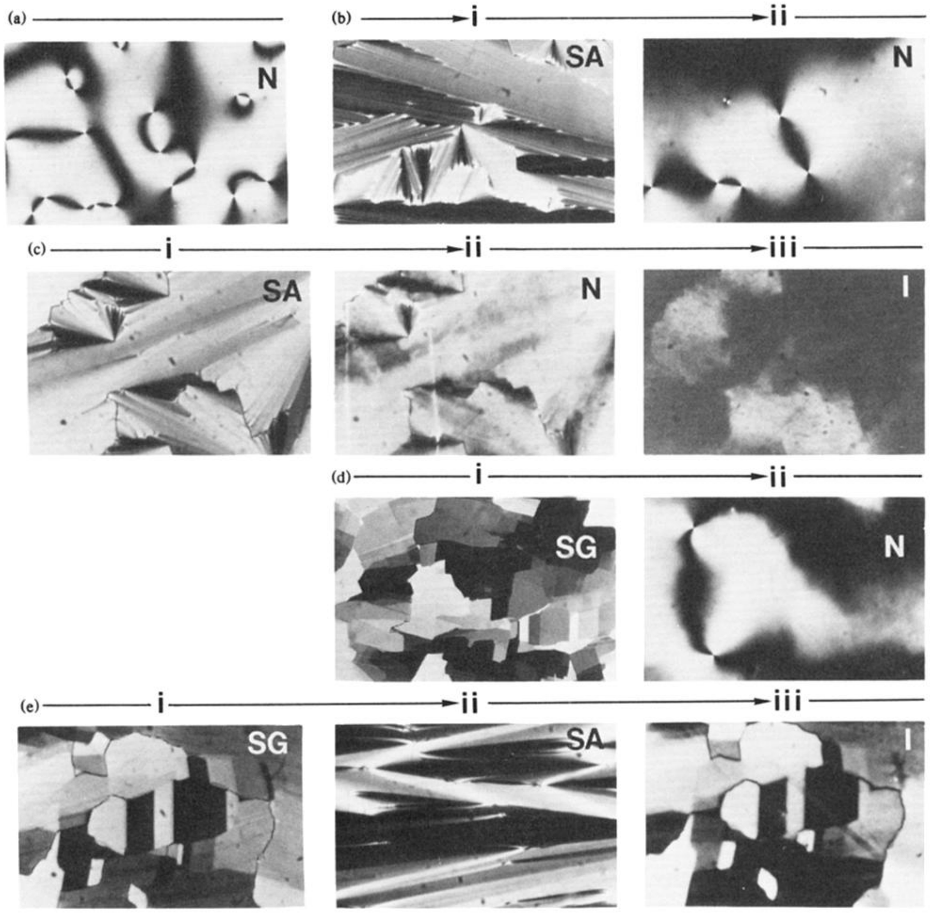
[3] The slides were cleaned by soaking in hot laboratory detergent solution and hot chromic acid followed by rinsing with microfiltered type-I reagent-grade water. Cleaned slides held vertically to dry would sheet water which would drain to micron-thick continuous films exhibiting the Newton color sequence. Slides were dried with use of filtered nitrogen and immediately coated.

[4] R. B. Meyer, in Proceedings of the Seventh International Liquid Crystals Conference, Bordeaux, France, 1-5 July 1978 (unpublished).

[5] J. C. Tarczon and K. Miyano, J. Chem. Phys. **73**, 1994 (1980).

[6] H. Yokoyama, S. Kobayashi, and H. Kamei, Mol. Cryst. Liq. Cryst. **99**, 39 (1983).

[7] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, London, 1974), Chap. 7.



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