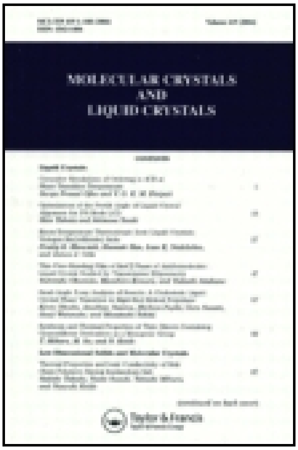

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Orienting Effects of Substrates on Cholesteryl Esters

Fraser P. Price [a] & Chan S. Bak [a]

[a] Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, 01002

Version of record first published: 21 Mar 2007.

To cite this article: Fraser P. Price & Chan S. Bak (1975): Orienting Effects of Substrates on Cholesteryl Esters, Molecular Crystals and Liquid Crystals, 29:2, 225-229

To link to this article: http://dx.doi.org/10.1080/15421407508083202

Mol. Cryst. Liq. Cryst., 1975, Vol. 29, pp. 225–229
© Gordon and Breach Science Publishers, Ltd.
Printed in Holland

Orienting Effects of Substrates on Cholesteryl Esters†

FRASER P. PRICE and CHAN S. BAK

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01002

(*Received March 22, 1974; in final form June 10, 1974*)

A given substrate favors a certain orientation of mesophase molecules at the substrate-mesophase interface. This favored orientation extends from the surface into the bulk of the mesophase, thus producing a certain thickness of uniform orientation. We selected five cholesteryl esters from the homologous series of aliphatic esters of cholesterol and studied the thicknesses of the uniformly oriented mesophases produced in fine glass capillaries. The inside walls of the capillaries were either bare glass or coated with thin films of various chemicals. The results show a wide variety in the thickness of uniform orientation depending upon the mesophase textures and the treatment of substrate surface.

It has long been known that substrates exert an orienting effect upon molecules of a liquid crystalline phase near the substrate-mesophase interface.[1a] These orienting effects of substrates have been utilized to obtain desired uniform liquid crystal textures. Various methods for preparing substrates have been reported; typically by rubbing a glass plate with lens paper or diamond powder,[1b] or by coating a glass plate with a thin film of chemicals.[2–4] The studies of orienting effects of substrates reported so far have been qualitative, merely concerned with whether the molecules are oriented parallel or perpendicular to the substrate-mesophase boundary. We report here our semi-quantitative investigations on how far the orienting effect extends from the surface into the bulk of the mesophase. Our study consists primarily of the observation of the maximum attainable thickness of a uniformly oriented mesophase produced inside a fine capillary tube. The thickness of uniform orientation is readily seen under a polarizing micro-

---

† This work was supported by grant No. HL13188 from the National Institutes of Health.

scope, and a further determination of the optical birefringence indicates how molecules are oriented on the substrate. This knowledge of the depth of orienting influence, we believe, is important because this will provide a criterion of the optimum distance between substrates necessary to obtain a uniformly oriented mesophase. It is also useful if one wishes to study liquid crystals in the absence of external perturbation, thus to avoid surface effects.

For a systematic study, five liquid-crystal formers were selected from the homologous series of aliphatic esters of cholesterol. These were the hexanoate, the nonanoate, the laurate, the myristate and the stearate. The choice was mainly governed by the desire to cover as wide a range of length of fatty acid as possible. Among the esters we studied, only the hexanoate has no smectic phase. The others exhibit both the cholesteric and smectic phases. The surfaces of the substrates (capillaries) we studied were pyrex glass, either bare or coated with thin films of hexadecyltrimethyl ammonium bromide (HTAB), N,N,-dimethyl-N-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP) or N-methyl-3-aminopropyl-trimethoxysilane (MAP).

EXPERIMENTAL

The cholesteryl esters and other chemicals we used were obtained from Aldrich Chemical Company (Hexanoate, Laurate), Eastman Chemical Company (Nonanoate, Myristate, HTAB), Applied Science Labs. (Stearate), and Dow Corning, courtesy of Dr. E. P. Plueddeman, (DMOAP, MAP). These latter were supplied with stock #XZ-2-2300 and XZ-2-2024 respectively. The cholesteryl esters were purified by recrystallizing once from *n*-pentanol, washing in methanol and drying under vacuum for several days until no further decrease in weight was observed.

The pyrex glass capillaries were drawn to several different bore radii in the range between 10-50 micron. The esters were introduced in the capillaries either without treatment or after coating the capillaries with HTAB, DMOAP, or MAP. The coating of the inside of the capillaries was done by first introducing a dilute solution (about 1% by volume in water for DMOAP and MAP, or in toluene for HTAB) and then drying in vacuum for several hours. For each ester-substrate pair, at least four capillaries at each bore radius were prepared. The capillaries, after being filled with esters, were embedded in epoxy resin supported between two parallel glass plates. This reduced the distortion of the microscope light beam by the cylindrical glass wall. The mesophase materials were then sheared axially along the tube, either by volume change on phase transition or by repeatedly changing the air pressure at one end of the sample. The sample was observed with a polarizing microscope to see changes in the thickness of uniform orientation.

By thickness of uniform orientation is meant the thickness of the annular region next to the wall where the mesophase exhibits a single crystal texture. The optic axis is either radial or axial. In all cases, the thickness increased as the shear was repeated until the thickness of uniform orientation reached a maximum value. This maximum thickness, we believe, is the distance the orienting effect of the surface can reach into the bulk for a given liquid crystal-substrate pair. With a capillary of bore radius smaller than the maximum thickness, a uniform alignment was produced all over the inside of the capillary. When the bore radius exceeded the maximum thickness, the molecules were aligned uniformly near the inside wall, but in the core region the texture was focal conic. The balance between the uniform domain and the focal conic domain appeared to be so delicate that frequently the focal conic texture projected into the uniform domain, thus resulting in a considerable variation in the thickness of uniform orientation. It was also interesting to note that sometimes a capillary of a certain bore radius produced a uniform orientation in the whole region, while a capillary with a smaller bore radius produced a uniform orientation near the wall and focal conic in the core region. This phenomenon is believed to reflect the variation in the orienting effect of a given substrate perhaps due to lack of sufficient experimental control over thickness of the deposited layer and the orientation of the molecules therein. The overall uncertainty in the determination of the thickness of the uniform orientation is about 50%. Within this uncertainty the orienting effect is found to be temperature-independent for a given mesophase. When a uniform alignment was obtained, the direction of molecular orientation was readily detectable by studying the optical birefringence with a polarizing microscope and quartz-wedge. When the samples are rotated 45° from the crossed polars direction in microscope, the uniformly aligned texture exhibits numerous color bands aligned parallel to the tube axis. The study of the wavelength and position of these color bands allows determination of the optical birefringence of the texture. Our results obtained on the birefringence of cholesteryl nonanoate are reported elsewhere.[5]

RESULTS AND DISCUSSION

Table I summarizes the observed effects of substrates upon the orientation and the maximum thickness of uniform orientation of the mesophases of the five cholesteryl esters studied. For both the smectic and cholesteric phases of a given ester, the glass surfaces and the MAP films produce orientation of the molecules parallel to the surface, while the HTAB and DMOAP films produce a perpendicular orientation. The parallel or perpendicular orientation of the molecules is inferred from the orientation of the optic axis in the uni-

TABLE I

Summary of the observed effects of substrates upon the thickness of uniform orientation of mesophases of the cholesteryl esters

Substrate	Orientation[a]	Mesophase	Hexanoate[b]	Nonanoate	Laurate	Myristate	Stearate
Glass	parallel	Cholesteric	20μ	50μ	15μ	5μ	10μ
		Smectic	xx	←	50μ		→
MAP	parallel	Cholesteric	←		10μ		→
		Smectic	xx	←	20μ		→
HTAB	perpendicular	Cholesteric	←		focal conic		→
		Smectic	xx	←	40μ		→
DMOAP	perpendicular	Cholesteric	←		focal conic		→
		Smectic	xx	←	40μ		→

(a) The orientation of the long axes of the molecules relative to the substrate surface.
(b) Smectic phase does not form in the Hexanoate.

formerly oriented region assuming that the direction of highest polarizability the cholesteryl ester lies along the major axis of the molecule. Thus, in the uniformly oriented region of a cholesteric phase where the optic axis is radial, because the molecular axes are perpendicular to the optic axis, the molecules are aligned parallel to the wall. In a smectic phase the optic axis of the liquid crystal and the molecular axes are in the same direction. Thus if in the uniformly oriented region the optic axis is radial, so are the molecules and hence the molecules are perpendicular to the wall. If the optic axis is axial in the capillary so are the molecules and hence they are parallel to the wall. The observed orientations are those that would have been predicted from the work of Kahn[3] and Guyon *et al*[6] for nematics.

It should be noted that the terms uniform orientation and focal conic refer to the experimentally observed situation, while the terms parallel and perpendicular refer to the inferred orientations of the molecules at the surface. Only with glass surface did the maximum thicknesses of uniform orientation differ markedly for five esters in the cholesteric phase ranging from 50μ for the nonanoate to 5μ for the myristate. There is no clear trend for the effect of ester length upon the thickness of uniform orientation. In the smectic phase on the glass substrate, the thicknesses are comparable (50μ) for all esters we studied. The MAP film produces a smaller thickness of uniform orientation than the glass surface, being for all the esters about 10μ in the cholesteric phase and 20μ in the smectic phase. The films of HTAB and DMOAP produce no uniform alignment in the cholesteric phase, but a good alignment of about 40μ thickness in the smectic phase. The poor efficiency of the MAP films in producing a uniform orientation of the mesophases may be partially due to the crude procedure we have employed to deposit the MAP film on the glass substrates. However, the films of HTAB and DMOAP obtained from the same deposition procedure as used with MAP produce much greater thickness of uniform orientation than the MAP film. One may further speculate that the apparently same deposition procedure actually produces films with different degrees of uniformity depending upon the deposition materials, and this results in different thicknesses of uniform orientation. Consideration of all these possibilities leads us to the conclusion that, using the deposition procedure described above in the Experimental Section, the mesophase-MAP interaction that produces parallel alignment is weaker in the smectic phase than the mesophase-substrate interactions that produce perpendicular alignment by the HTAB or DMOAP.

We also conclude that the alignment is always less efficient in the cholesteric phase than in the smectic phase. This indicates that the substrate-cholesteric phase interaction is weaker than the substrate-smectic phase interaction. A possible qualitative explanation for this weak interaction between the substrate and cholesteric phase is that some of the molecular forces such as dipole moment that produce interaction with the substrate are averaged out (or reduced) in the cholesteric phase where the succeeding layers are twisted and form a helical structure. Thus it might be expected that a cholesteric phase with a long helical pitch has a stronger interaction with the substrate than one with a short pitch, and the strongest interaction occurs when the pitch length is infinity (smectic phase).

References

1a. P. Chatelain, *Bull. Soc. franc. Min. Crist.*, **66**, 105 (1943).
1b. D. Berryman, *Phys. Rev. Lett.*, **28**, 1683 (1972).
2. C. Williams, P. Pieranski, and P. Cladis, *Phys. Rev. Lett.*, **29**, 90 (1972).
3. F. J. Kahn, *Appl. Phys. Lett.*, **22**, 386 (1973).
4. L. T. Creagh and A. R. Kmetz, *4th Int. Liq. Cryst. Conf.*, Kent, Ohio (August 21–25, 1972).
5. F. P. Price and C. S. Bak, *Cylindrically Symmetric Textures in Mesophases of Cholesteryl Esters*, presented at the American Society Meeting in August, 1973 at Chicago, Illinois.
6. J. E. Proust, L. Ter-Minassian-Saraga, and E. Guyon, *Solid State Comm.*, **11**, 1227 (1972).