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

Anonmalous Spherulitic Crystallization from a Cholesteric Mesophase

John O. Lephardt [a] & Bernard J. Bulkin [a]
[a] Department of Chemistry, Hunter College of the City University of New York, New York, 10021
Version of record first published: 21 Mar 2007.

To cite this article: John O. Lephardt & Bernard J. Bulkin (1973): Anonmalous Spherulitic Crystallization from a Cholesteric Mesophase, Molecular Crystals and Liquid Crystals, 24:1-2, 187-189

To link to this article: http://dx.doi.org/10.1080/15421407308083398

Molecular Crystals and Liquid Crystals. 1973. Vol. 24, pp. 187–189

Printed in Great Britain

Anomalous Spherulitic Crystallization from a Cholesteric Mesophase

JOHN O. LEPHARDT and BERNARD J. BULKIN

Department of Chemistry
Hunter College of the City University of New York
New York, New York 10021

Received November 13, 1972

Abstract—A ring crystallization pattern has been observed for a mixture containing 80% cholesteryl nanoate–20% cholesteryl propionate. This is discussed in terms of a segregation of components originating in the smectic phase of the nanoate.

As part of a continuing program of spectroscopic studies of liquid crystals we recently had occasion to prepare samples of a mixed cholesteric mesophase containing 80% cholesteryl nanoate – 20% cholesteryl propionate (by weight). When this mixture is allowed to crystallize over a 24 hour period from the cholesteric phase (approximately 47°) the well developed ring pattern shown in Fig. 1 is obtained. This effect is seen every time this phase crystallizes from the isotropic phase. It is not observed for films deposited from petroleum ether solution.

The initial film thickness in the cholesteric phase is approximately 25 microns. The maximum height of the rings is about 100 microns. The ring spacing as measured from the photographs is 0.2 mm.

If the initial cholesteric film is too thin (<10 microns) or too thick (>100 microns) the ring pattern is not observed. In addition, the weight ratio of the two components must be in the range 90 : 10 to 70 : 30 nanoate : propionate.

This ring pattern is indicative of segregation of the two components by diffusion. Of interest is the driving force for such segregation. We know that it must be considerable to achieve a 0.2 mm spacing in a 24 hour period. The two materials readily coexist in the cholesteric mesophase, however, which would indicate similar chemical potentials and only weak segregation forces.

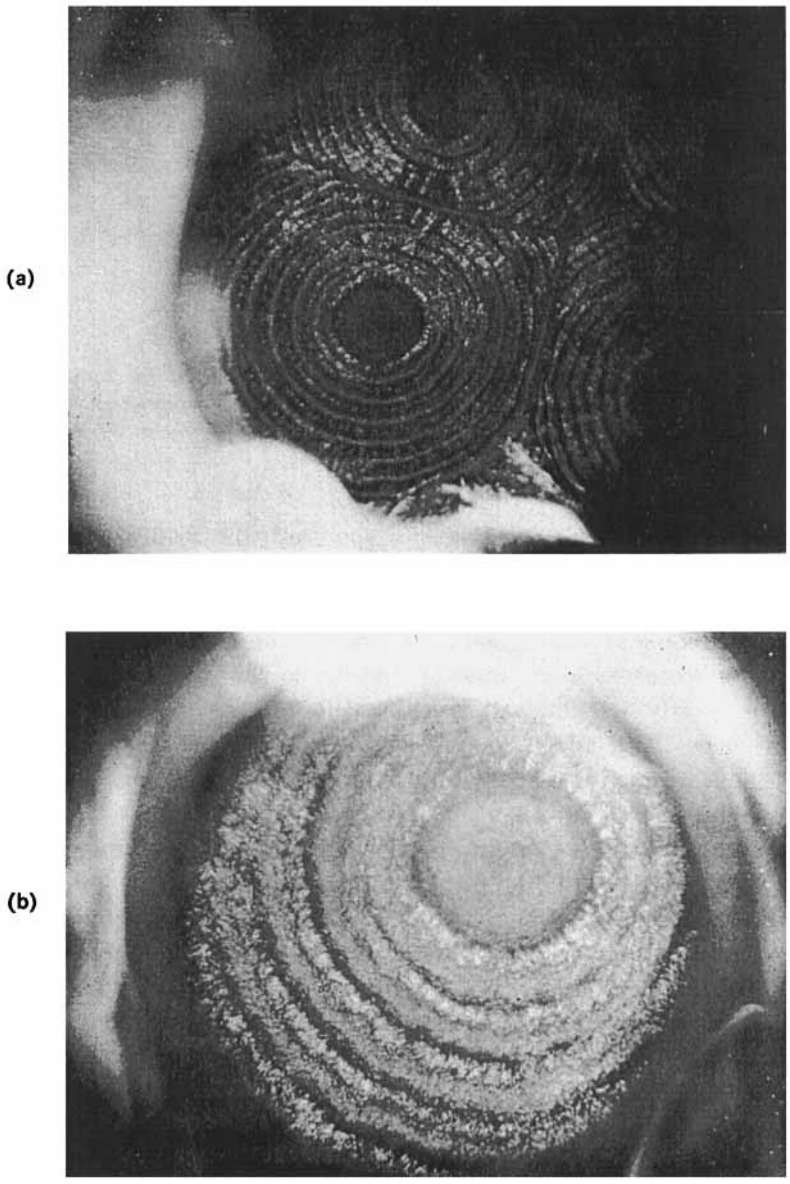

Figure 1. Ring crystallization of an 80% cholesteryl nanoate–20% cholesteryl propionate mixture. (a) Magnification 25 ×. (b) Magnification 50 ×.

We believe that this driving force for segregation lies in the existence of a smectic phase for cholesteryl nanoate but not for cholesteryl propionate. As the cholesteric phase cools, the nanoate can achieve a thermodynamically more stable state by excluding the propionate, forming a pure smectic phase. At higher concentrations of propionate the smectic phase is suppressed and crystallization proceeds directly from the cholesteric phase. At low propionate concentrations the nanoate accommodates the "impurity" in the smectic phase.

This result indicates the importance of the smectic mesophase for long alkyl chain cholesteric materials, and is consistent with the recent phase diagram for mixed cholesteric phases determined by Porter.[1]

We acknowledge support of the U.S. Army Research Office–Durham. Several helpful discussions of our observation took place with colleagues at the IVth International Liquid Crystal Conference.

REFERENCE

1. R. Porter, presented at the IVth International Conference on Liquid Crystals, Kent, Ohio, August, 1972.