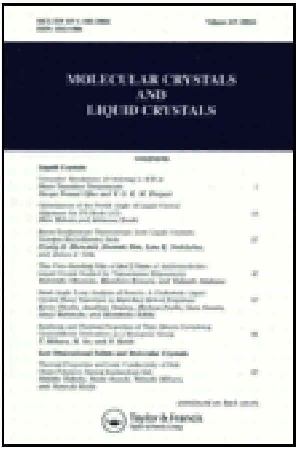


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Order in Diacetylenic Microstructures

P. E. Schoen [a] , P. Yager [a] , J. P. Sheridan [a] , R. Price [a] , J. M. Schnur [a] , A. Singh [b] , D. G. Rhodes [c] & S. L. Blechner [c]

[a] Bio/Molecular Engineering Branch, Code 6190 Naval Research Laboratory, Washington, D.C., 20375-5000

[b] Geo-Centers, Inc., Ft. Washington, MD, 20744

[c] University of Connecticut Health Center, Farmington, CT, 06032

Version of record first published: 13 Dec 2006.

To cite this article: P. E. Schoen , P. Yager , J. P. Sheridan , R. Price , J. M. Schnur , A. Singh , D. G. Rhodes & S. L. Blechner (1987): Order in Diacetylenic Microstructures, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 357-366

To link to this article: http://dx.doi.org/10.1080/00268948708074550

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 357-366
Photocopying permitted by license only

Printed in the United States of America

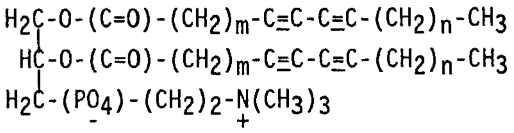
ORDER IN DIACETYLENIC MICROSTRUCTURES

P.E. SCHOEN[1], P. YAGER[1], J.P. SHERIDAN[1], R. PRICE[1], J.M. SCHNUR[1], A. SINGH[2], D.G. RHODES[3] AND S.L. BLECHNER[3]
1. Bio/Molecular Engineering Branch, Code 6190
Naval Research Laboratory, Washington, D.C. 20375-5000
2. Geo-Centers, Inc., Ft. Washington, MD 20744.
3. University of Connecticut Health Center, Farmington, CT 06032

Abstract Polymerizable diacetylenic lipids form a long, hollow tubular bilayer microstructure tnat has been characterized by microscopy, spectroscopy and x-ray diffraction. The lipid monomers are highly ordered at the molecular level, and at high density the microstructures themselves align giving macroscopic order.

INTRODUCTION

Our laboratory (NRL) has been characterizing polymerizable lipids and the microstructures they form, particularly diacetylenic lecithins such as 1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine[1,2]. A number of these lipids have been synthesized,[3] containing diacetylenic moieties in their two identical hydrocarbon chains whose positions can be specified by the number of methylene groups between the carboxyl and diacetylene groups (m), and between the diacetylene and terminal methyl groups (n). Hence the aforementioned compound is designated $DC_{8,9}PC$. The general formula is:



$$\begin{array}{l} H_2C\text{-}O\text{-}(C{=}O)\text{-}(CH_2)_m\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_n\text{-}CH_3 \\ \;\;HC\text{-}O\text{-}(C{=}O)\text{-}(CH_2)_m\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_n\text{-}CH_3 \\ H_2C\text{-}(\underset{-}{PO_4})\text{-}(CH_2)_2\text{-}\underset{+}{N}(CH_3)_3 \end{array}$$

The lipids we have synthesized include DC$_{8,9}$PC and other homologs of the form DC$_{m,n}$PC in which C$_{m,n}$ are C$_{10,13}$,[4] C$_{5,13}$, C$_{6,13}$, C$_{7,9}$, C$_{10,9}$, C$_{10,7}$,[5] and C$_{8,7}$. We have also synthesized a series of lipids with a total of 27 carbons in their hydrocarbon chains , including C$_{5,16}$, C$_{6,15}$, C$_{7,14}$, C$_{8,13}$, C$_{9,12}$, C$_{10,11}$, and C$_{11,10}$.[3] The diacetylenic groups render these lipids polymerizable by ultraviolet light and other forms of radiation.[6]

The lipids, DC$_{m,n}$PC, have been shown to form tubular microstructures by two distinct routes, a thermal technique, and by precipitation. In the thermal formation technique, DC$_{8,9}$PC forms bilayer and multibilayer liposomes in aqueous dispersion above its hydrocarbon chain melting temperature, as measured in excess water (T$_m$ of 43 °C). These liposomes are unstable at lower temperatures; on gradual lowering of the temperature to about 38 °C, they can convert quantitatively to hollow "tubules".[7-9] Dimensions vary from 0.4 to 1 micrometer in diameter and tens to several hundreds of micrometers in length, with walls that vary from two to about ten bilayers in thickness; i.e. 10 to 50 nm. Tubules may also be formed by precipitation from solution in organic solvent, such as methanol, ethanol, isopropanol, and propylene glycol.[10] To form the microstructures, a solution of lipid in solvent was formed, to which water was added in one of several ways, including slow dripping and dialysis. The number and length of the tubules formed depended upon the concentration of lipid and the quantity and rate of water addition, i.e. the rate of crystallization. The average tubule lengths could be controlled by this method from 10 to 15 microns up to hundreds of microns.

Another lipid morphology formed by the precipitation technique was an open helix, shown in Figure 1, having a pitch and a diameter of about 0.5 to 1.0 microns.[2] The ribbon of lipid forming the helix has a variable width, resulting in a range of structures from open helices to continuous tubules. The helices were all right handed when made from lipid with the naturally-occurring L chiral headgroup,[10] and both left and right handed when formed from a mixture of L and D material.[11] To facilitate visualization of the fragile helical structures in a manner that allowed the handedness of the helices to be observed, samples in water were coated with a thin layer (20-30 nm) of copper metal by an electroless deposition process.

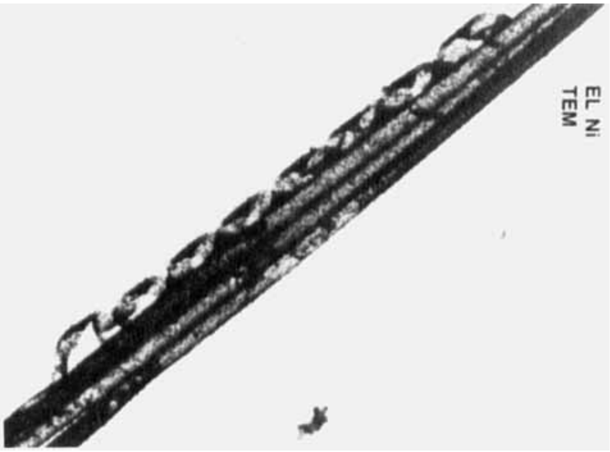


Figure 1. Electron micrograph of tubules and helices.

The microstructures can be polymerized by a 1,4 addition reaction between adjacent diacetylene moieties.[12] The requirement for adjacency is a stringent one for the polymerization of diacetylenic materials.[13] Polymerization of these lipids is observed only when they are highly ordered, in the low temperature phase when the hydrocarbon chains are usually in the all-trans configuration.

DISCUSSION

A considerable effort has been underway in our laboratory for the past three years to understand the forces for formation and the structure of diacetylenic lipid microstructures. Although the crystal structure of the tubules and helices has not been solved, results from polymerization and microscopy, spectroscopy and x-ray small angle diffraction indicate that they are highly ordered over macroscopic distances.

Tubules can be polymerized, as noted above, and while this process does not go to completion (50 to 80% elimination of monomer),[3] it does indicate a substantial amount of long range coherence in the polymer: polarized optical microscopy reveals the strength of absorption by the chromophore is uniform over an entire tubule, encompassing distances of many microns, without any sign of grain boundaries or other defects. Transmission electron microscopy of a polymerized tubule shows a helical pattern of fibrous material in the tubule wall,[1] and helical ripples on the tubule surface.[2] A simple explanation for this texturing is a change in the lipid packing caused by the polymerization, distorting the arrangement of the monomer units. Again, the pattern is relatively uniform over the full diameter of the tubule, indicating large scale coherence in the underlying molecular structure.

The Raman spectra of monomeric tubules have been investigated in considerable detail.[14,15] Of particular interest is the low frequency region containing the longitudinal acoustic modes (LAM)[16,17] resulting from longitudinal vibration of all-trans segments of the alkyl chains. These are spectral features that are not typically seen in lipid samples, or are observed only with great difficulty even in lipids with high chain order and tight packing. In the case of diacetylenic lipid tubules intense LAMs were recorded, possibly the most intense ever observed in a hydrated phospholipid.

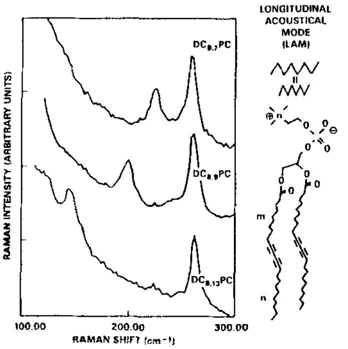


Figure 2. Raman LAM bands for a homologous series of diacetylenic lipids with the tubule morphology.

As is shown in Figure 2, two LAMs are observed, indicating possible decoupling of the LAM vibrations of the upper (m) and lower (n) alkyl segments. In Figure 2 spectra are shown for three tubule forming lipids: $DC_{8,7}PC$, $DC_{8,9}PC$ and $DC_{8,13}PC$. One band at 262 cm^{-1} is common to each, while the other occurs near 230 cm^{-1} for $DC_{8,7}PC$, 194 cm^{-1} for $DC_{8,9}PC$ and 144 cm^{-1} for $DC_{8,13}PC$. This lower frequency band varies in a manner consistent with the expected inverse relationship of LAM frequency to alkyl chain segment length, n. Association of the higher frequency band at 262 cm^{-1}

with the m segment must await further experimentation with another homologous series of lipids in which m is varied systematically. These observations are of special interest, since they suggest the possibility of observing separately the phase behavior of the upper and lower segments of the alkyl chains. In addition, observation of such LAMs argues strongly for a high degree of order in the case of tubule morphology.

Thin sheets of lipid material were formed by centrifugation of tubule dispersions and examined by small angle x-ray diffraction.[18-20] The signal from the multilayers was strong and yielded lamellar diffraction to 16th order, indicating that the material was highly ordered. The d-spacing (unit cell dimension in the bilayer normal direction) for $DC_{8,9}PC$ at 84% humidity was 64.7 A for unpolymerized samples and 67.5 A for polymerized

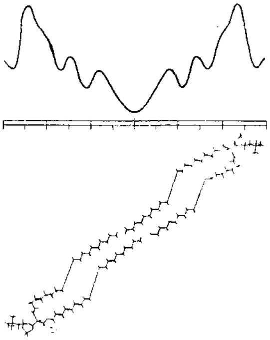


Figure 3. $DC_{8,9}PC$ monomer electron density profile. Scale is normal to the bilayer surface and has magnitude = d. Molecular models show possible orientation of two lipid molecules spanning the bilayer, tilted 35° with respect to the normal.

material. By comparison dipalmitoyl phosphatidylcholine, which is 7 carbon atoms shorter (two 7-carbon segments in the all-trans configuration in a bilayer would account for about 15 A), has a d-spacing of about 60 A. This apparent discrepancy in thicknesses might be explained by a model which assumes a tilt of the $DC_{8,9}PC$ lipid chain axis of about 35° with respect to the bilayer surface normal, and two carbon interdigitation at the bilayer center, as shown in Figure 3.

If this model for the structure is correct, the d-spacing for $DC_{8,11}PC$ would be predicted to be 70.7 A, a value which compares favorably with the preliminary experimental spacing of 71.1 A.[16]

The large number of orders of diffraction observed in the data, and the interdigitation required by molecular modeling to fit the data are further evidence that the tubules are a very highly ordered system.

TUBULE ORDERING

Our discussion thus far has dealt with the molecular structure of diacetylenic lipids. We conclude by noting that the high aspect ratio of the tubule microstructure makes it highly likely that at sufficient density an ensemble of tubules could be expected to display coherent orientation. Figure 2 shows an example where this appears to be the case. The tubules also can be aligned by flow in a viscous medium,[10] and by the imposition of a sufficiently high magnetic field (>10 kGauss).[21]

In summary, the diacetylenic lipids have a number of remarkable and potentially useful properties. They display mesomorphic behavior on two levels: at the molecular level the lipid monomers in water dispersion form liposomes of liquid crystalline bilayers, that at low temperatures self-assemble into tubules, and the tubules themselves, in the multiple micron size range, will self-align at sufficiently high number densities. In addition the tubules have a hollow core that is accessible for the encapsulation of other materials, and inside and outside surfaces that can be decorated with fluorophores, metal, polymer, etc. The metal coats yield a durable, conducting cylinder (ferromagnetic, in the case of nickel coating) that can be incorporated into and oriented in a polymer matrix. The resulting composites are expected to have useful mechanical, optical/electromagnetic and other properties.

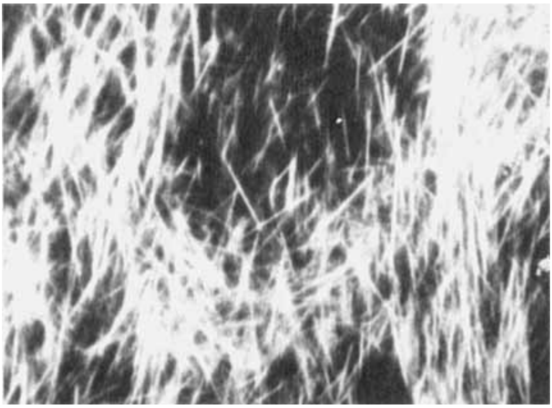


Figure 4. Ordering in densly packed tubules.

ACKNOWLEDGEMENTS

Our thanks to Ms. Barbara Herendeen for synthesis of some of the lipids used, and to Mr. Jacque Georger and Ms. Angela

Weaver for laboratory assistance in the formation and characterization of the tubules. This work was supported by the Defense Advanced Research Projects Agency, which we acknowledge with gratitude.

REFERENCES

1. P. Yager and P.E. Schoen, Mol. Cryst. Liq. Cryst., 106, 371-381, (1984).

2. P. Yager, P.E. Schoen, C. Davies, R. Price, and A. Singh., Biophys. J., 48, 899-906, (1985).

3. A. Singh; B.P. Gaber; B. Singh; R.R. Price, T.G. Burke; P.E. Schoen, J.M. Schnur; P. Yager; in "Surfactants in Solution", K.L. Mittal, ed., Elsevier Press. in press.

4. A. Singh, R.B. Thompson, J.M. Schnur, J. Am. Chem. Soc., 108, 2785-2787, (1986).

5. A. Singh, J.M. Schnur, Polym. Preprint, 26, 184-185, (1985).

6. D.S. Johnston, S. Sanghera, M. Pons and D. Chapman, Biochim. Biophys. Acta, 602, 57-69, (1980).

7. P. Yager, R.R. Price, J.M. Schnur, P.E. Schoen, A. Singh, and D.G. Rhodes, submitted to Chem. Phys. Lipids.

8. T.G. Burke, A. Singh and P. Yager, Ann. N.Y. Acad. Sci., in press

9. A.S. Rudolph and T.G. Burke, Biochim. Biophys. Acta., in press.

10. J.H. Georger, R.R. Price, A. Singh, J.M. Schnur, P.E. Schoen and P. Yager, J. Am. Chem. Soc., in press.

11. A. Singh, T.G. Burke, J.M. Calvert, J.H. Georger, B. Herendeen, R.R. Price, P.E. Schoen, and P. Yager., submitted to J. Am. Chem. Soc.

12. G. Wegner, Z. Naturforsch., 24b, 824, (1969).

13. R.H. Baughman and R.R. Chance, Ann. NY Acad. Sci., 313, 705, (1978).

14. P.E. Schoen, P. Yager and R.G. Priest, Polydiacetylenes: NATO Advanced Study Institute, Stratford on Avon, 1984, (1985).

15. J.P. Sheridan, NRL Memorandum Report #5975, Conformational Order in Lipid Tubules Formed From a Diacetylenic Lipid: A Raman Spectroscopic Study, in press.

16. G. Vergoten, G. Fleury and Y. Moschetto, Advances in Infrared and Raman Spectroscopy Vol. 4, (Eds. R.J.H. Clark and R.E. Hester, Heyden, U.K., 1978).

17. B.P. Gaber and W.L. Peticolas, Biochim. Biophys. Acta, 465, 260 (1977).

18. L. Herbette, J. Marquardt, A. Scarpa and J. Blasie, Biophys. J., 20, 245 (1977).

19. E.N. Serralach, R. Dijkman, G.H. de Haas and G.G. Shipley, J. Mol. Biol., 170, 155 (1983).

20. D.G. Rhodes, S.L. Blechner, P. Yager and P. Schoen, submitted.

21. C. Rosenblatt, P. Yager and P. Schoen, Biophys. J., in press.