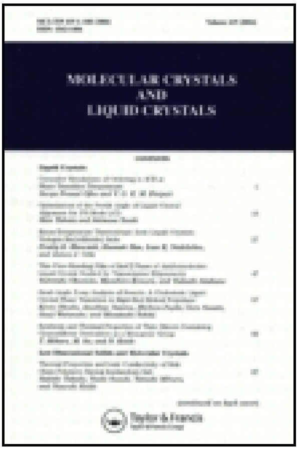

Molecular Crystals and Liquid Crystals

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

Biaxial Ordering of Melted Chains Near the Gel Phase Transition: an NMR Study

Nuno A. P. Vaz [a c] , J. William Doane [a] & Mary E. Neubert [b]

[a] Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, U.S.A.

[b] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, U.S.A.

[c] Centro de Fisica da Materia Condensada, Lisbon, Portugal

Version of record first published: 14 Oct 2011.

To cite this article: Nuno A. P. Vaz , J. William Doane & Mary E. Neubert (1981): Biaxial Ordering of Melted Chains Near the Gel Phase Transition: an NMR Study, Molecular Crystals and Liquid Crystals, 68:1, 11-22

To link to this article: http://dx.doi.org/10.1080/00268948108073548

Mol. Cryst. Liq. Cryst., 1981, Vol. 68, pp. 11–22
0026-8941/81/6801-0011 $06.50/0

Biaxial Ordering of Melted Chains Near the Gel Phase Transition: an NMR Study†

NUNO A. P. VAZ‡ and J. WILLIAM DOANE
Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 U.S.A.

and

MARY E. NEUBERT
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 U.S.A.

(*Received September 16, 1980*)

A new phase in the simple lipid bilayer system (potassium palmitate-water) in the vicinity of the L_α to gel phase transition is studied using deuterium magnetic resonance. In this phase the hydrocarbon chains are observed to remain melted but become biaxially ordered. Measurements of the motionally averaged quadrupole coupling constant and of the motionally induced asymmetry parameter were made as a function of temperature and are interpreted in terms of orientational order parameters. The analysis shows that the principal feature of the phase transition is the onset of a transverse long range orientational order of the chains in the plane of the bilayer while the order of the chains in the direction normal to the bilayer remains little affected. This order is suggestive of a cooperative tilted arrangement of the melted chains in the bilayer. The uniaxial-biaxial phase transition is observed to be of first order.

INTRODUCTION

The transition to the gel phase of lamellar phases has been of considerable interest in recent years since it is believed to play a role in the function of biological membranes.[1] On a molecular level, the transition has generally been regarded as one in which the hydrocarbon chains change from a melted state

---

† Presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

‡ On leave from Centro de Fisica da Materia Condensada, Lisbon, Portugal.

to a frozen state upon cooling through the transition.[2] In addition, x-rays[3,4] have shown that in some lipids there is a decrease in interlayer spacing which has been attributed to either a cooperative tilt or an overlap of hydrocarbon chains within the bilayer. We have recently reported the existence of a new lamellar phase in the (70% potassium palmitate-30% water) system near the temperature normally regarded as the gel transition. The phase was detected by the onset of a motionally induced asymmetry in the deuterium magnetic quadrupole spectral pattern from the hydrocarbon chain region of the molecule and interpreted in terms of biaxial orientational order.

This paper describes a detailed NMR study of this new phase and of the associated uniaxial-biaxial phase transition. In this study the terminal end segment of the hydrocarbon chain (methyl group) was selectively deuterated for the deuterium magnetic resonance (DMR) study. This particular segment of the molecule was chosen for study because it is most sensitive for the DMR observation of biaxiality, a property brought on by a cooperative tilt or some other asymmetry arrangement of the molecules in the bilayer.[6] Also, since this segment is on the end of the chain, is sensitive to changes in the orientational order of the chain which occurs at the transition.

The results of this study show a region of about 10° C in the vicinity of the liquid crystal-gel transition where, on the time scale of the DMR measurement, there is little significant change in the orientational order of the terminal hydrocarbon segment about the bilayer normal indicating that the chains remain in the same melted state as the L_α phase at the transition. Also in the new phase there is a strong biaxial component as observed and measured by an asymmetry parameter on the DMR spectral pattern. At the uniaxial-biaxial phase transition there is found to be a two-phase region about 5° wide indicating the transition to be one of first order in contrast to those phase transitions which have been reported in the L_α phase at higher temperatures in this same system.[5] At temperatures below the biaxial phase another two phase region occurs with the lower temperature phase appearing to be one where the order of the hydrocarbon chain is freezing out.

The measured quantities in the experiment are the time averaged coupling constant and asymmetry parameter of the deuterium electric quadrupole interaction as well as the strength of the magnetic dipole-dipole interaction observed as a slight broadening on the quadrupole spectra. These time averaged quantities are discussed in terms of orientational order parameters which are in turn related to various other aspects of the motion of the hydrocarbon chain in the biaxial phase and at the uniaxial-biaxial transition.

MATERIALS AND METHODS

Potassium palmitate (16, 16, 16-d_3) was prepared by heating a mixture of 500 mg (1.93 mmoles) palmitic acid (16, 16, 16-d_3) (Merck), 124 mg KOH and 0.25 ml D_2O at 60° C with stirring for 5 min. The dried solid was recrystallized from abs EtOH (using several filtrations to remove insoluble materials) to give 376 mg (65.9%) of the salt. The sample was then prepared by making a mixture of potassium palmitate with 30% by weight of water and mixing according to a procedure described elsewhere.[5,7]

The sample was placed in a magnetic field of strength 30.8668 MHz for deuterium (Nalorac superconducting magnet) and the quadrupole echo technique was used to obtain the spectra.[8] The probe head was equipped with a computer controlled temperature regulator in which the temperature gradient across the sample was less than 0.2° C. The gel phase transition was approached from above and, at the expected temperature of the gel transition,[4] 50° C, a mixed phase region was observed which appeared to be inhomogeneous and not in equilibrium. Upon further cooling to 44° C a single phase and stable DMR spectral pattern was achieved as shown in Figure 1c which is easily recognized as a typical biaxial powder pattern.[7] The experiment would then proceed either by further cooling the sample or by raising the temperature and eventually crossing a two phase region (Figure 1b) and reaching the lamellar L_α phase (Figure 1a); the spectral pattern of Figure 1a identifies a uniaxial distribution and is characteristic of all L_α phases above 50° C.[8] Data obtained for the gel phase in a cooling cycle agreed with the data acquired in the heating cycle apart from a small hysteresis which is usual for these systems which exhibit a two-phase region.[4]

The two-phase region was homogeneous and stable only on the heating cycle. The inhomogeneity and instability on the cooling cycle may be tentatively explained as a consequence of there being a tendency for the formation of a small fraction of free water[10] as well as two separate phases which are not in equilibrium. After some time, self-diffusion of the water brings the two-phase region into equilibrium to produce a homogeneous system. The two-phase region is a result of the two component feature of this system as expected by the Gibbs Phase Rule.[4,9]

Data were acquired to a temperature of about 10° C below the phase transition where the spectral pattern abruptly decreased in intensity. This was believed to be due to a broadening of the pattern reducing the signal into the noise beyond detection of the instrument. Even the singularities could not be detected in the broadened spectrum, indicating that some of the asymmetry was retained, destroying the *edge* singularities characteristic of Figure 1a.

RESULTS AND DISCUSSION

The deuterium quadrupole interaction can be observed as a perturbation on the Zeeman interaction. In this case, a spin of I = 1 gives rise to a spectrum of two lines with a splitting given by:[11]

$$\delta\nu_Q = \frac{3}{2}\nu_Q\left[\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right) + \frac{\eta}{2}\sin^2\theta_0\cos2\phi_o\right], \qquad (1)$$

where θ_0 and ϕ_0 are the spherical coordinate angles giving the direction of the applied magnetic field in the frame of the principal-axis system of the electric field gradient. The quantity ν_Q is the quadrupole coupling constant defined in the usual manner.[11] In a liquid crystal phase, the measured coupling constant, ν_Q^{lc}, is usually a much smaller value than that observed in the solid phase, ν_Q^s, where the orientation of the molecule and its individual segments are rigidly fixed.[11] The measured values of ν_Q^{lc}, at a particular site in the molecule of a liquid crystal phase is a time average of its corresponding value in the solid phase and gives information regarding the orientational motion and order of the segment of the molecule at that site. The quantity η is the asymmetry parameter.[11] In a liquid crystal, η^{lc} is only observed in those phases which are biaxially ordered.[6,12,13] Its value is a reflection of the asymmetry of the orientational order and motion in these phases and can be present in a liquid crystal even though it may be absent in the solid phase of the same system, which is the case in this study.

Equation (1) is convenient only for aligned bilayer samples. For unaligned samples there is an isotropic distribution in the orientation of the principal axis system and hence of the angles θ_0 and ϕ_0. This distribution gives rise to a spectral pattern, the shape of which depends on the value of η.[14,15] The shapes of spectral patterns for $\eta^{lc} = 0$ and $\eta^{lc} = 0.5$ were calculated following Ref. 15 and are illustrated in Figures 1a and 1b (right traces), respectively, where a small amount of dipole broadening to the quadrupole spectral lines was included; the broadening was taken as Gaussian with a line width of $\delta\nu_D = 120 \pm 20$ Hz or $\delta\nu_D = 430 \pm 80$ Hz respectively. The details of the line broadening effects (i.e. Gaussian or Lorentzian) were found to be only of secondary importance in the fitting results.

In the uniaxial patterns there are basically no shape fitting parameters other than a small contribution from $\delta\nu_D$ which only rounds off sharp corners and edge singularities on the theoretical spectral patterns. The splitting between the 90° singularities gives the value ν_Q^{lc}.[14] In the biaxial patterns the edge singularities become logarithmic singularities and are more easily rounded off by $\delta\nu_D$.[15] The splitting between the singularities and the overall shape is now governed by both η^{lc} and ν_Q^{lc}. Each of these parameters has a different effect on the shape and their values are easily obtained from a shape fitting procedure.

In the two-phase region the spectral patterns (illustrated in Figure 1b) are a combination of both uniaxial and biaxial ones, and it becomes necessary to include an additional fitting parameter which gives the relative amount of each phase present. The percentage of uniaxial phase in the two-phase region, P_u, has been calculated from the theoretical reconstruction of each spectrum and proportional to the ratio of the area under the uniaxial spectral distribution and the area under the total spectrum. In Figure 1b, right trace, $P_u = 50.13\%$. In this same figure the other fitting parameters are: $\nu_Q = 4.00 \pm 0.02$ kHz and $\delta\nu_D = 120 \pm 20$ Hz for the uniaxial distribution,

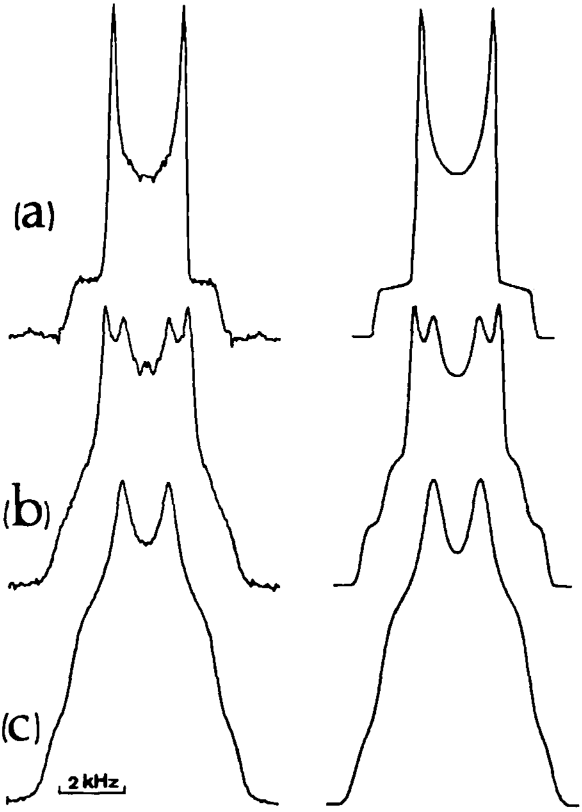

FIGURE 1 Deuterium spectra at 30.8668 MHz of potassium palmitate-d_3 in a lamellar dispersion containing 30% by weight of water and taken at three different temperatures are shown in the left-half of the figure. They are characteristic isotropic powder patterns representative of the a) uniaxial phase at 60° C with 10,800 scans, b) two phase region at 47.63° C with 20,000 scans, and c) biaxial phase at 44.75° C with 41,000 scans. Each spectral width is 8 KHz. The right-half of the figure shows the corresponding simulated DMR powder patterns. The parameters used to generate these simulated spectra are given in the text.

and $\nu_Q = 6.00 \pm 0.05$ kHz and $\delta\nu_D = 300 \pm 40$ Hz for the biaxial distribution.

The temperature dependence of the measured asymmetry parameter and the relative contribution of the uniaxial phase to the total mixture in the two-phase region are given in Figure 2a. The temperature dependence of ν_Q^{lc} obtained from fitting the spectral patterns is given in Figure 2b. In both figures the arrows indicate the transition temperatures as calculated from extrapolation to 0 and 100% of the straight line that best fits the experimental values of P_u. They are observed to agree very well to those observed experimentally.

In order to examine molecular models for this biaxial phase, it is useful to express the data in terms of orientational order parameters which describe

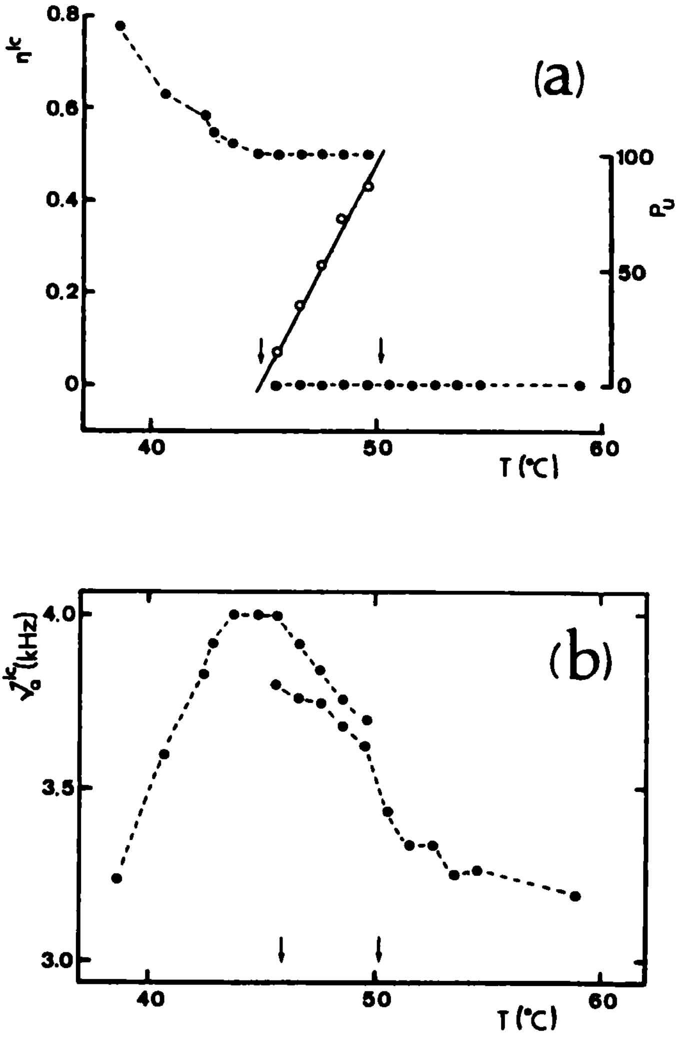

FIGURE 2 a) Temperature dependence of the asymmetry parameter, η^{lc}, (solid dots, left vertical axis) and of the percentage of uniaxial phase in the two phase region, P_u, (open circles, right vertical axis). Broken lines are drawn to aid the eye. Arrows indicate the onset of the two-phase region. b) Temperature dependence of the time averaged quadrupolar coupling constant as determined from the theoretical fits. Arrows indicate the onset of the two-phase region.

various aspects of the motion of the hydrocarbon chain and its biaxial order. In this interpretation we first of all apply a simple model used in our earlier studies of the L_α phases above the gel transition.[13] In discussing this transition it is convenient to first of all discuss the temperature variation of the time averaged coupling constant.

A Motional averaging of ν_Q

In the principal axis frame for the orientational order the coupling constant in the liquid crystal, ν_Q^{lc}, is related to that in a solid by the equation (see Appendix A):

$$\nu_Q^{lc} = \nu_Q^{s}(s_{0,0}S_{0,0} + \tfrac{3}{4}s_{0,2}S_{0,2}) \tag{2}$$

where ν_Q^s is the coupling constant of the terminal methyl group measured in the solid state at a temperature where the group is still rotating about the terminal C—C bond. Because of the three-fold nature of this bond, there is no asymmetry associated with this interaction in the solid where the group is under rotation. The conformational averages, $s_{0,m}$, and the molecular order parameters, $S_{0,m}$, are given by:

$$s_{0,0} = \langle \tfrac{3}{2}\cos^2\beta - \tfrac{1}{2} \rangle \qquad S_{0,0} = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle$$
$$s_{0,2} = \langle \sin^2\beta \cos 2\alpha \rangle \qquad S_{0,2} = \langle \sin^2\theta \cos 2\psi \rangle$$

where θ and ψ are the polar angles which give the orientation of the principal z-axis, M_z of the molecular frame relative to the principal z-axis of the time averaged field gradient. M_z is fixed to the fluctuating molecule and is its most ordered axis (essentially the long axis). The parameter $S_{0,0}$ gives the degree of order of the molecular long axis whereas $S_{0,2}$ gives the anisotropy in the order of that axis. The angles β and α give the orientation the terminal C—C bond relative to the molecular frame. It is normal procedure to fix the molecular frame to the most ordered segment (α position of the chain). Under this choice the conformation parameters, $s_{0,m}$ reflect the relative orientation of the terminal segment relative to the α-position.

Equation (2) is only valid for a suitably chosen molecular frame (principal molecular axis frame); otherwise, there would be additional order parameters and additional terms in that equation. Furthermore, it is known that Eq. (2) may be valid for one liquid crystal phase whereas insufficient for another phase in the same system in that there can occur a change in the orientation of the principal axis frame relative to the molecule introducing added terms at the transition. Although we did not specifically test for this possibility, the temperature dependence of ν_Q^{lc}, in Figure 2 does not seem to indicate that such is the case for the uniaxial-biaxial transition. At this transition the temperature dependence of ν_Q^{lc}, follows the same upward trend exhibiting only a small discontinuity which could be a discontinuous change in either $s_{0,2}$ or $S_{0,1}$ instead of the onset of an off-diagnonal parameter.

Below the two-phase region, the value of $\delta\nu_Q$ is seen to decrease. It does not seem reasonable that this could be due to the first term in Eq. (2) as that would simply further decrease in the order of the chain either through more averaging of $s_{0,0}$ or $S_{0,0}$. A more likely cause of the observed decrease in $\delta\nu_Q$ would be through an increase in $S_{0,2}$ where, if the second term of Eq. (2) were of opposite

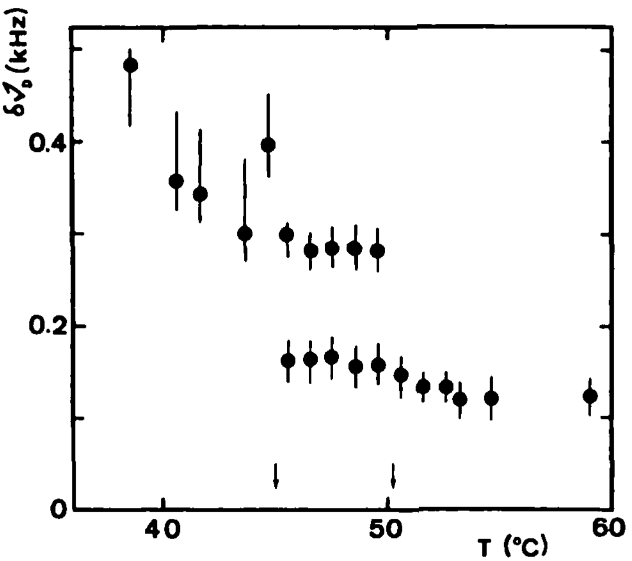

FIGURE 3 Temperature dependence of the dipolar broadening. The error bars reflect the spread in $\delta\nu_D$ necessary to fit at the best either the peaks or the shoulders of the powder patterns. The dipolar width was taken to be constant (frequency independent). Arrows indicate the onset of the two-phase region.

sign, it would subtract from the first term to decrease the sum. From a physical point of view an increase in $S_{0,2}$ is quite reasonable if the chains are tilted in the bilayer. This is because fluctuations in the orientation of the long axis can become more anisotropic in tilted layers as fluctuations in one direction cause a modulation in the thickness of the bilayer which is energetically less favorable than in a perpendicular direction which does not. Likewise, opposite signs for the first and second terms in Eq. (2) is also reasonable in that they were found to be of opposite sign in a study of the $L\alpha$ phase[13] and also because a change in the principal molecular axis frame at the transition to the biaxial phase does not appear to be likely.

B The asymmetry parameter, η^{lc}

The motionally induced value of η^{lc} in terms of orientational order parameters has been examined in previous publications.[6,7,12] From Appendix A the asymmetry parameter can be expressed as:

$$\eta^{lc} = \frac{\frac{3}{2}\nu_Q^s(s_{0,0}S_{2,0} + 2s_{0,2}S_{2,2})}{\nu_Q^{lc}} \tag{3}$$

where $S_{2,0} = <\sin^2\theta\cos 2\phi>$ describes the degree of cooperativity in the anisotropic fluctuation of the long axis. The angle ϕ is the third Euler angle

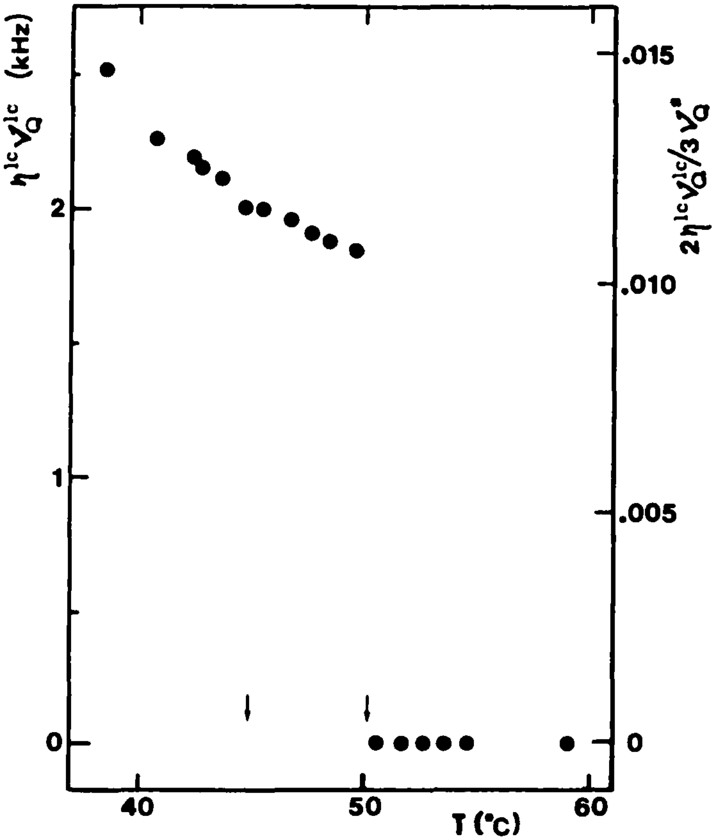

FIGURE 4 Temperature dependence of the biaxial order parameters as indicated by $\eta^{lc}\nu_Q^{lc}$. Arrows indicate the onset of the two-phase region.

introduced by the second principal axis of the biaxial system. The other parameter $S_{2,2} = \frac{1}{2}<(1 + \cos^2\theta)\cos2\phi\cos2\psi - \cos\theta\sin2\phi\sin2\psi>$ describes a long range order in M_y and M_x.

It is seen from Eq. (3) that the increase in η^{lc} with temperature is primarily due to the decrease in ν_Q^{lc} which appears in the denominator. The biaxial order is proportional to the product $\eta^{lc}\nu_Q^{lc}$ which is shown in Figure 4. There is little temperature dependence in this order other than the discontinuity at the phase transition. Without further data (patterns from other segments) it is not possible to separate the relative contribution of these two biaxial terms. Both terms are clearly present in that $S_{2,2}$ would only vanish for a cylindrically shaped molecule or a phase where there was free rotation, and the presence $S_{0,2}$ rules out this possibility. It is possible that one could have a non-tilted phase with the same two parameters present; however, the fact that tilted phases have been identified in thermotropic liquid crystals tends to favor the tilted model.

CONCLUSIONS

These data show the presence of a first order uniaxial-biaxial transition near the temperature which has been classified as the gel transition. The transition is into a phase where the hydrocarbon chains are melted in the bilayers. At a lower temperature there appears to be another transition where the hydrocarbon chains freeze out. A uniaxial pattern has been observed for the frozen chains.[16]

One possible model for the uniaxial-biaxial phase transition might be one where, in the uniaxial phase, there is cooperative tilt within the bilayers but no cooperativity between bilayers such that self-diffusion[17] between bilayers would cause the phase to appear uniaxial on the average. At the transition, the onset of cooperativity between bilayers would cause the phase to appear biaxial in the NMR experiment.

A similar experiment is currently under way to examine the gel transition in the hydrocarbon chains of phospholipids where a tilted structure has been suggested for the temperature region between the upper and lower transitions in these compounds.[18] Biaxial order of the head group in phospholipids in the gel phase has been observed in ^{31}P NMR by others.[19]

Acknowledgment

This work was supported in part by the National Science Foundation under grant number DMR79-04393.

References

1. S. Marcelja and J. Wolfe, *Biochim. Biophys. Acta,* **557,** 24-31 (1979).
2. a) J. F. Nagle, *Ann. Rev. Phys. Chem.,* (to appear).
   b) J. F. Nagle and H. L. Scott, *Physics Today,* **31,** N.2, 38-47 (1978).
3. M. J. Janiak, D. M. Small and G. G. Shipley, *Biochemistry,* **15,** 4575-4580 (1976).
4. A. Skoulios, *Adv. Colloid Int. Sci.,* **1,** 79-110 (1967).
5. N. A. P. Vaz, J. W. Doane and M. E. Neubert, *Phys. Rev. Lett.,* **42,** 1406-1409 (1979).
6. D. Allender and J. W. Doane, *Phys. Rev. A,* **171,** 1077-1080 (1978).
7. N. A. P. Vaz and J. W. Doane, *Phys. Lett.,* **77A,** 325 (1980).
8. a) I. Solomon, *Phys. Rev.,* **110,** 61-65 (1958).
   b) J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic and T. P. Higgs, *Chem. Phys. Lett.,* **42,** 390-394 (1976).
9. See for example: H. B. Callen, *Thermodynamics* (John Wiley and Sons, London, 1960) p. 165.
10. R. R. Balmbra, D. A. B. Bucknall and J. S. Clunie, *Mol. Cryst. Liq. Cryst.,* **11,** 173-186 (1970).
11. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

12. J. W. Doane in *Magnetic Resonance of Phase Transitions*, ed. F. Owens (Academic Press, New York, 1979) p. 171.
13. N. A. P. Vaz, J. W. Doane and M. E. Neubert, *Phys. Rev. A* (to appear, 1980).
14. M. H. Cohen and F. Reif, *Solid State Physics*, **5**, (Academic Press, New York, 1957) pp. 321-438.
15. N. Bloombergen and T. J. Rowland, *Acta Met.*, **1**, 731-746 (1953).
16. J. H. Davis and K. R. Jeffrey, *Chem. Phys. Lipids*, **20**, 87-104 (1977).
17. P. Ukleja and J. W. Doane, *Proceedings of the Intl. Conf. on Ordering in Two Dimensions*, Geneva, Wisconsin (1980).
18. P. W. Westerman, M. J. Vaz and J. W. Doane, *Federation Proceedings of the Biophys. Soc.*, New Orleans **39**, 2190 (1980).
19. a) P. R. Cullis and M. J. Hope, *Bioch. Bioph. Acta*, **597**, 533-542 (1980).
    b) R. G. Griffin, *J. Am. Chem. Soc.*, **98**, 851-853 (1976).
20. D. J. Photinos, P. J. Bos, J. W. Doane and M. E. Neubert, *Phys. Rev. A*, **20**, 2203-2212 (1979).

Appendix A

The nuclear spin quadrupole interaction for deuterium is measured on perturbation on the Zeeman interaction in the presence of an applied magnetic field. From Eq. (9) of Ref. 20 the time averaged quadrupole Hamiltonian when expressed in the same frame as the Zeeman interaction is written as:

$$< \mathcal{H}_Q > = \frac{h\nu_Q^s}{4I(2I-1)}[3I_z^2 - I(I+1)]\,D_{m,0}(\theta_0, \phi_0)\,R_m$$

where $R_m = <D^*_{m,m'}(\phi, \theta, \psi)> <D^*_{m',0}(\alpha, \beta, \gamma)>$ and where $\nu_Q^s = e^2q^sQ/h$ is the quadrupole coupling constant associated with the deuterated methyl group which is rotating about the terminal C—C bond and as measured in the solid state where the electric field gradient q^s is not further time averaged by fluctuations in orientation of the terminal C—C bond but there is still rotation about the C—C bond axis.

In the principal axis frame of the time averaged field gradient of the liquid crystal $m = 0$ and ± 2 only and the polar angles θ_0 and ϕ_0 give the orientation of that principal axis frame relative to the direction of the applied magnetic field. The time dependent Euler angles $\phi(t)$, $\theta(t)$ and $\psi(t)$ give the orientation of the molecular frame (which is fixed to some rigid segment of the molecule) relative to the principal axes of the time averaged field gradient. The angles $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ give the orientation of the C—C bond of the terminal methyl group relative to the molecular frame.

When treated as a perturbation on the Zeeman interaction, to the first order, the splitting for $I = 1$ becomes:

$$\delta\nu_Q = \nu_Q^s[A(\tfrac{3}{2}\cos^2\theta_0 - \tfrac{1}{2}) + B\sin^2\theta_0\cos 2\phi_0].$$

Where, if we also choose a suitable orientation for the molecular frame on the molecule (principal molecular axis frame for the orientational order) then $m' = 0$ and ± 2 and A and B are given:[20]

$$A = \tfrac{3}{2}(s_{0,0}S_{0,0} + \tfrac{3}{4}s_{0,2}S_{0,2})$$

and

$$B = \tfrac{9}{8}(s_{0,0}S_{2,0} + 2s_{0,2}S_{2,2})$$

where

$$\begin{array}{ll} S_{0,0} = <\tfrac{3}{2}\cos^2\beta - \tfrac{1}{2}> & S_{0,0} = <\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}> \\ S_{0,2} = <\sin^2\beta\cos 2\alpha> & S_{0,2} = <\sin^2\theta\cos 2\psi> \\ & S_{2,0} = <\sin^2\theta\cos 2\phi> \\ & S_{2,2} = \tfrac{1}{2} < \tfrac{1}{2}(1 + \cos^2\theta)\cos 2\phi\cos 2\psi \\ & \qquad - \cos\theta\sin 2\phi\sin 2\psi>. \end{array}$$

We can now define a time averaged quadrupole coupling constant, ν_Q^{lc}, and asymmetry parameter, η^{lc}, for the liquid crystal phase relative to these values in the solid phase as:

$$\nu_Q^{\mathrm{lc}} = \tfrac{2}{3}A\,\nu_Q^s$$

and

$$\eta^{\mathrm{lc}} = \frac{2B}{A} = \frac{4}{3}B\left(\frac{\nu_Q^s}{\nu_Q^{\mathrm{lc}}}\right)$$