

A Novel Method for the Alignment of Lyotropic L_α Phases in Magnetic Fields

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An ionically charged L_α phase can be prepared without shear by mixing a small amount of methylformiate to a L_3 phase from alkyldimethylaminoxide, hexanol, and water. If the structural transformation induced by the hydrolysis reaction of the ester is carried out in the presence of a high magnetic field, a macroscopically aligned lamellar phase is obtained. The alignment process was studied by ^2H NMR measurements. The NMR measurements allow the estimation of the time constant of the alignment process, and at the same time, they can be used to control the degree of macroscopic orientation of the system.

Introduction

The complete alignment of lyotropic mesophases is of interest both for fundamental studies of their anisotropic properties and for the use of such phases in material science for various applications. Several methods are known today with which multidomain phases can be aligned to a completely oriented macroscopic phase. It is known, for instance, that multidomain $L_{\alpha h}$ phases can be aligned by shear into macroscopically aligned phases. The dynamics and the degree of alignment have been studied by small-angle neutron scattering (SANS) measurements in shear flow.¹ Furthermore, it has been demonstrated that $L_{\alpha h}$ phases under special conditions can be aligned by surface forces exerted from the wall of the container.² Macroscopically aligned samples with a thickness of several centimeters have been observed. In such cases, the alignment usually takes several days to go to completion. It is also known that nematic phases of the disk and cylindrical type can be aligned in magnetic fields.³ Depending on the composition of the phase and the type of counterions, the director of the phase can orient either perpendicular or parallel to the magnetic field.⁴ Nematic disklike phases are usually found in ternary phase diagrams at lower and higher cosurfactant concentration than the lamellar phases ($L_{\alpha h}$).⁵ In such situations, it is possible to pass from the nematic phase into the lamellar phase simply by a decrease of the temperature. If the transformation of the nematic phase into the $L_{\alpha h}$ phase is carried out in a magnetic field, aligned lamellar phases can be obtained.⁶ Detailed measurements have shown that at first the nematic phase, which usually is a low-viscosity phase, is completely aligned and then in the aligned state is transformed into the aligned lamellar phase whereby the directors of both phases stay in the same direction. Magnetically aligned $L_{\alpha h}$ phases have been used to study the conductivity anisotropy of the phases,⁷ and in systems in which dye molecules had been incorporated into the surfactant bilayers, it was possible to determine the order parameter of the dye molecules.⁸ Up to now, this magnetically induced orientation process was restricted to systems in which the phase transition from one phase to another phase can be induced by temperature changes. Therefore, only a few systems are suited for magnetic orientation.

In this manuscript, we report on a new method to prepare completely aligned lamellar phases ($L_{\alpha h}$). It is based on the

recently made observations that multidomain $L_{\alpha h}$ phases are produced when the bilayers of sponge phases (L_3) are ionically charged by a chemical reaction in the stagnant system.⁹ By this strategy, several virgin $L_{\alpha h}$ phases have been prepared that had not been exposed to shear prior to their formation. During this transformation, the surfactant system passes from a single-phase system through a two-phase system to another single-phase system. The phase transition is too fast for a macroscopic phase separation of the intermediate system. In the two-phase state, separated small domains of a $L_{\alpha h}$ phase are floating in a continuous low-viscosity L_3 phase. Exposure of this state to a strong magnetic field (several tesla) leads to a completely aligned $L_{\alpha h}$ phase. However, if the $L_{\alpha h}$ phase formation takes place without the magnetic field, a subsequent orientation by the magnetic field is either impossible or strongly suppressed. Thus, the $L_{\alpha h}$ phase is only aligned when it is formed in the status nascendi in a magnetic field. The fact that the outlined procedure of in situ methylformiate hydrolysis in a magnetic field leads to an oriented lamellar phase makes magnetically induced alignment accessible for a whole new class of systems.

Phase Preparation of the Lamellar Phase

The experiments were carried out on the known ternary phase diagram of tetradecyldimethylaminoxide (TDMAO)/hexanol/water.¹⁰ In Figure 1, the phase diagram of the cosurfactant/surfactant ratio against the surfactant concentration is given. As other similar phase diagrams with a zwitterionic surfactant and a cosurfactant, it shows the sequence of phases L_1 , $L_1/L_{\alpha l}$, $L_{\alpha l}$, $L_{\alpha l}/L_{\alpha h}$, $L_{\alpha h}$, $L_{\alpha h}/L_3$, L_3 with increasing cosurfactant/surfactant ratio.¹¹ In this diagram, the L_α region is split into two subregions, which are named $L_{\alpha l}$ and $L_{\alpha h}$. These two regions have different macroscopic properties and different morphologies. The $L_{\alpha l}$ phase is a vesicle phase, and the $L_{\alpha h}$ phase is the lamellar phase. The sponge phase, L_3 , is an optical isotropic phase with a low viscosity and shows a characteristic narrow existence region of the cosurfactant/surfactant ratio.¹⁰ The characteristic structure of the sponge phase is shown in a freeze fracture transmission electron microscopy (FF-TEM) image (Figure 3a): bicontinuous, interpenetrating systems of water channels that are separated from each other by surfactant membranes.

It has been shown previously that the sponge phase (L_3) in the shown phase diagram (Figure 1) becomes unstable when the neutral bilayers of the L_3 phase are ionically charged with

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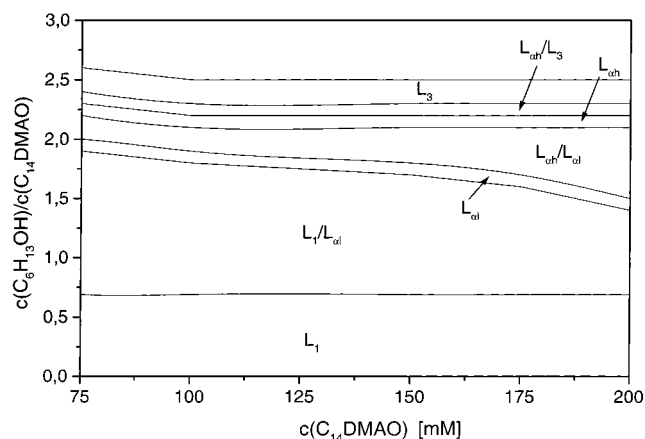


Figure 1. Phase diagram of tetradecyldimethylaminoxide (TDMAO)/hexanol/water in a plot of the cosurfactant/surfactant ratio against the surfactant concentration. It shows the sequence of phases L_1 , L_1/L_α , L_α , $L_\alpha/L_{\alpha h}$, $L_{\alpha h}$, $L_{\alpha h}/L_3$, L_3 .

a few percent of ionic surfactants.¹² When the charging process is done by mixing a small amount of a solution of an ionic surfactant with the L_3 phase, then immediately a viscoelastic phase with densely packed vesicles is obtained. If however the charging is carried out by releasing protons in the quiescent L_3 phase, that is, without shear stress, the result is a birefringent stacked $L_{\alpha h}$ phase without vesicles.¹³ The release of protons and the subsequent protonation of the alkylaminoxide molecules can be done by adding small amounts of methylformiate to the

L_3 phases. The ester is soluble in the L_3 phase, and its lifetime is long enough to ensure that the mixing process has no influence on the hydrolysis. In the hydrolysis reaction, methylformiate dissociates into formic acid and methanol. The formic acid protonates the aminoxide surfactant headgroups. After 10% of the alkyl dimethylaminoxide surfactant is transformed into cationic surfactant, the transition from the L_3 phase to the lamellar phase occurs. The presence of OH^- ions in the L_3 phase is responsible for a pH value of 8 at the beginning of the transformation from the L_3 phase to the lamellar phase. The hydrolyzation of methylformiate into formic acid and methanol decreases the pH value to pH = 7. In Figure 2, we demonstrate the transformation of the sponge phase (L_3) into the birefringent L_α phase by a series of photos of samples between crossed polarizers. The photos were taken at different times after the methylformiate had been added to the L_3 phase. After 20 min, the first birefringent speckles can be seen, which become larger and more intense with time. The hydrolysis reaction is completed within 1 day. Assuming a first-order process for the formation of the lamellar phase, the fraction of the birefringent lamellar phase visible on the photos can be used to determine the rate constant of the reaction. A detailed evaluation needs to take the varying thickness of the sample into account. Here, we took a simpler approach for a rough estimate of the rate constant from the photos: We used the reciprocal value of the time after which no significant changes of the visible appearance took place as three times the rate constant (i.e., 98.5% of the reaction is completed). After 60 min, the refraction pattern is nearly constant, which gives a rate constant of $k = 1/1200 \text{ s}^{-1}$.

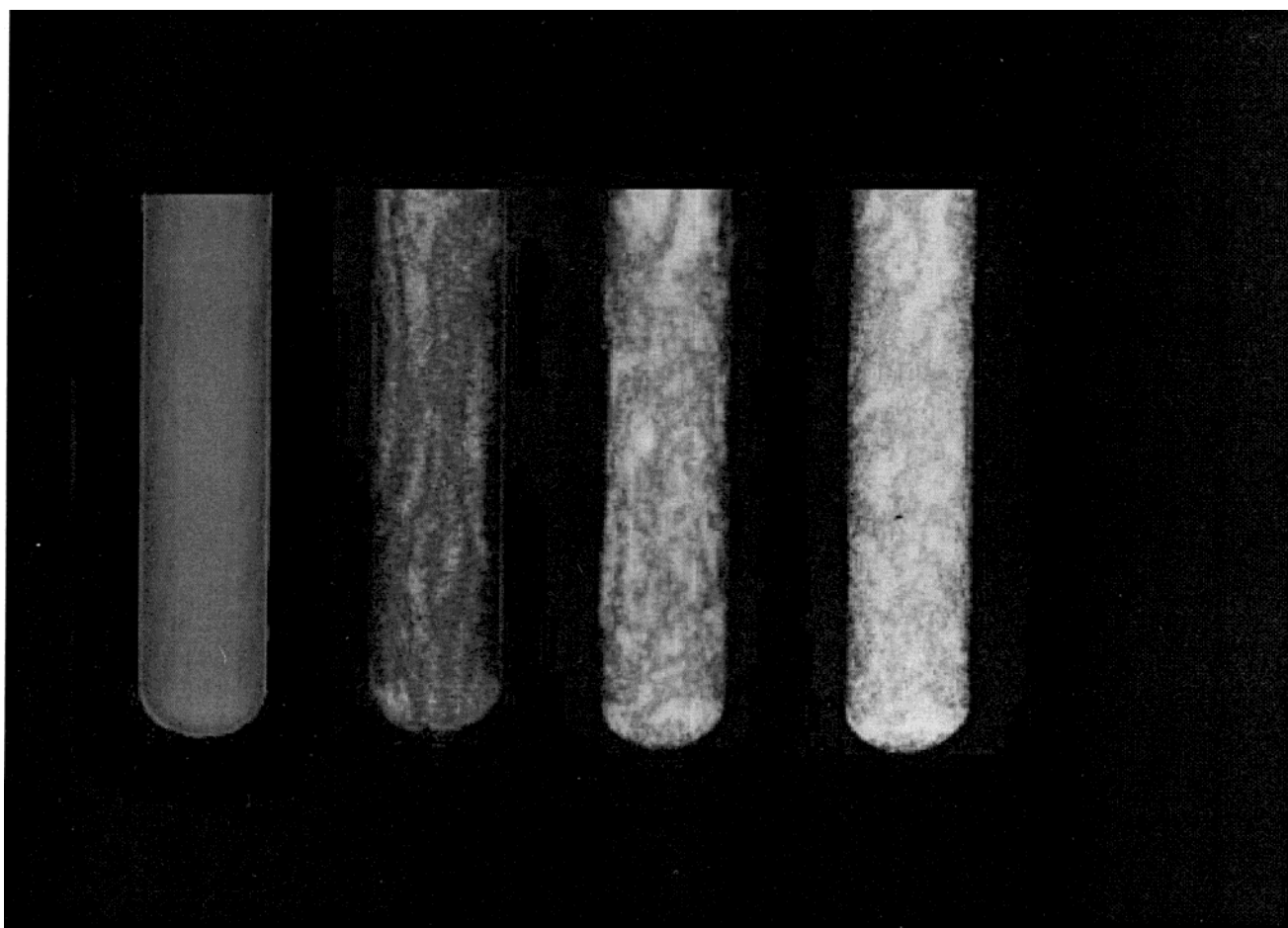


Figure 2. Development of the birefringence with time in a sample of 100 mM TDMAO, 250 mM hexanol, and 10 mM methylformiate: from left to right, after 8, 20, 30, and 90 min.

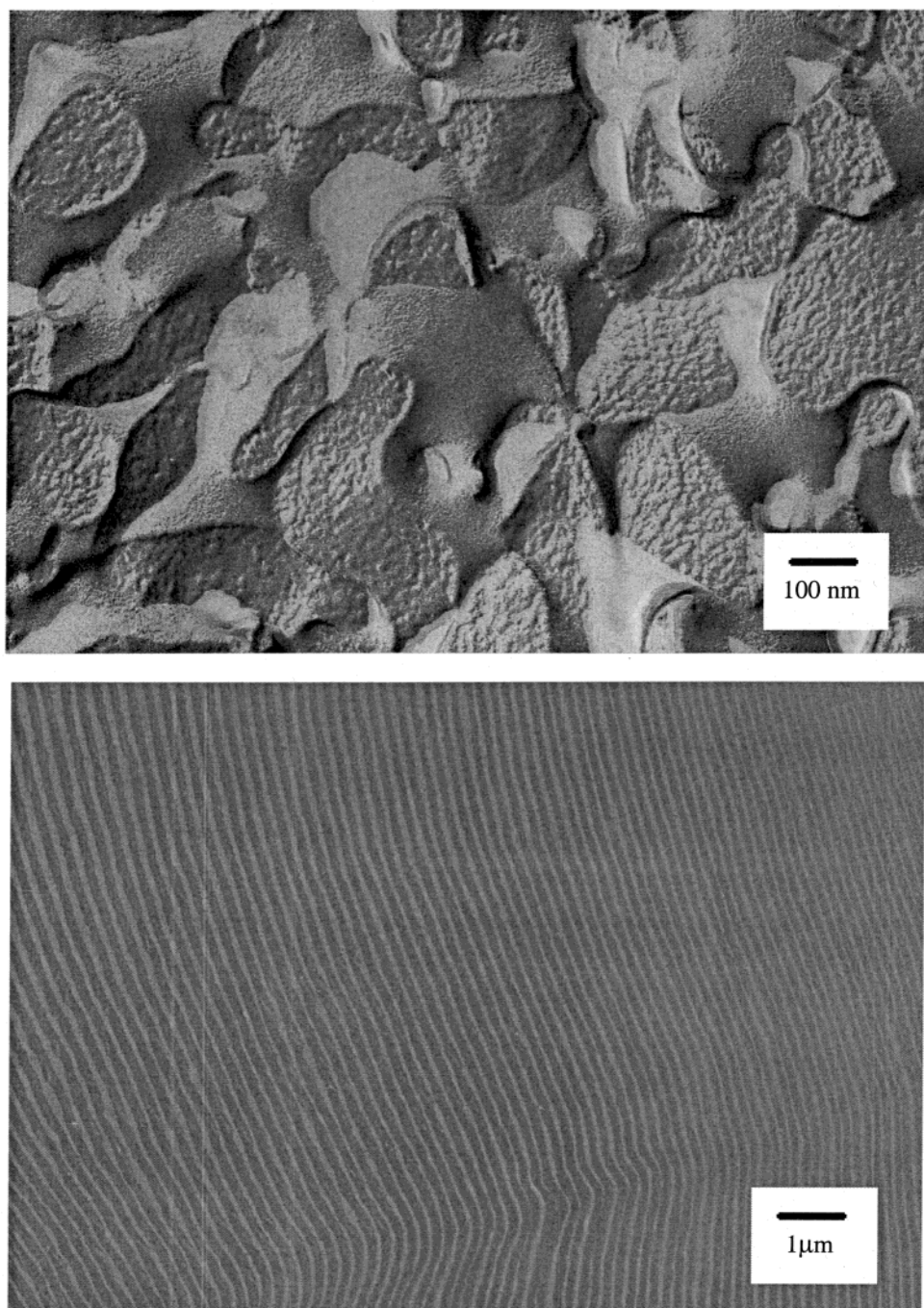


Figure 3. Electron micrographs (a) from the sponge phase (L_3) (100 mM TDMAO/250 mM hexanol) and (b) from the lamellar phase ($L_{\alpha h}$) (100 mM TDMAO/250 mM hexanol/10 mM methylformiate).

The corresponding image of the morphology of the aggregate structure of the lamellar phase ($L_{\alpha h}$) with its staggered bilayers is displayed in Figure 3b. The lamellar phase presents parallel bilayers with weak undulations. The interlamellar spacing evaluated from the electron micrograph picture is approximately 50 nm. A comparison with Figure 3a shows the different structure of both phases.

NMR Characterization of the Lamellar Phase

The NMR line shape is dominated by the interaction of the electric quadrupole moment of a given ^2H nucleus (spin $I = 1$) with its local electric field gradient (EFG) originating in molecules from the charge distribution in the corresponding

chemical bond. The resulting spectrum contains information on the distribution of the orientation of the EFG tensor with respect to the external magnetic field.¹⁴ In many cases, the principal axis of the EFG tensor is parallel to the axis of the $\text{C}-^2\text{H}$ σ bond. Because of the orientation dependence of the NMR frequency, molecular dynamics has a strong impact on the ^2H NMR spectrum. In isotropic phases, the fast molecular motions average the quadrupolar interactions to zero, and a single sharp central peak is observed in the spectrum. In liquid crystalline phases, the quadrupolar interaction is not averaged to zero, and a residual contribution is retained. In the case that the director is oriented in a magnetic field, that is, in a sufficiently fluid system, a doublet is observed. In the case of rapid anisotropic translational and rotational motions, which occur within the

anisotropic geometries of the individual aggregates, a time-averaged quadrupolar interaction leads to a reduced quadrupolar splitting.¹⁵ Thus, the quadrupolar splitting depends on the order parameter of the deuterated molecules and the molecular motions in the individual phase.¹⁶

A sample containing microcrystallites randomly oriented with respect to the external magnetic field gives a powder-type spectrum, that is, a Pake spectrum. The spectrum is the result of the superposition of the distribution of pairs of lines, whereas aligned liquid crystalline domains lead to a spectrum that shows only pairs of sharp lines, in the most single case just one pair.

In the following ^2H NMR spectra, we studied the transformation of the sponge phase (L_3) into the birefringent lamellar phase (L_α) by recording the ^2H NMR spectra of the samples at different times after adding methylformiate to the sponge phase (L_3). All ^2H NMR spectra were obtained by applying a solid echo pulse sequence with $\pi/2$ pulse lengths of $2.6\ \mu\text{s}$ and a $40\ \mu\text{s}$ interpulse delay in a magnetic field of $9.3\ \text{T}$.

The different phases can be classified by their typical quadrupolar splitting spectra of D_2O or of other deuterated molecules in the sample.^{16,17} Here, we show the ^2H NMR spectra of samples using either α -deuterated hexanol- d_2 or D_2O . The alcohol hexanol is used as a cosurfactant. It is an essential component of the different phases and known to facilitate the formation of the lamellar lyotropic phase.^{17,18} Thus, it allows monitoring of the ordering of the aggregates much more directly than D_2O . Measuring, in addition, the D_2O spectra allows one to sensitively probe the anisotropic character of the water in the aggregates. In other words, one is able to clarify the question of whether a fully aligned phase is formed.

The ^2H NMR spectrum of the sponge phase (L_3), the starting point of the kinetic reaction, is given in Figure 4a. The unconstrained, that is, isotropic, rapid motion of the hexanol molecules in the L_3 phase results in vanishing of a time-averaged quadrupolar interaction leading to a central Lorentzian without quadrupolar splitting.

The result of a self-assembly of lyotropic liquid crystals without external fields is a random distribution of domain orientations. Those samples show the characteristic Pake spectrum, consisting of the superposition of the signals of all different domain orientations. Such a NMR spectrum of a TDMAO system 24 hours after adding methylformiate to the sponge phase (L_3) is shown in Figure 4b. Hexanol- d_2 molecules that are not incorporated into the lamellar bilayers but are dissolved in the aqueous phase lead to the additional central peak. The exposure of such a randomly aligned lamellar phase to a magnetic field of $9.3\ \text{T}$ for $48\ \text{h}$ is nearly without influence on the measured NMR spectra. Therefore, a subsequent orientation is either strongly suppressed or impossible (Figure 4b, dotted line).

However, if the transition from the sponge phase (L_3) to the lamellar phase ($L_{\alpha h}$) takes place in a strong magnetic field ($9.3\ \text{T}$), the NMR spectra obtained are significantly different, showing two sharp lines (Figure 4c). The progress of the phase transformation can be directly monitored by ^2H NMR. The NMR spectra shown in Figure 5 are averaged over 256 scans. Each scan takes about $1\ \text{s}$. Within $530\ \text{s}$ after adding methylformiate to the sponge phase (L_3), a weak doublet in addition to the central line can be seen (Figure 5). This doublet corresponds to α -deuterated hexanol- d_2 molecules that are incorporated in the aligned liquid crystalline domains. With ongoing reaction, the intensity of this doublet structure is increasing, while at the same time the intensity of the central peak is decreasing. Consequently, during the reaction, the NMR spectrum is a superposi-

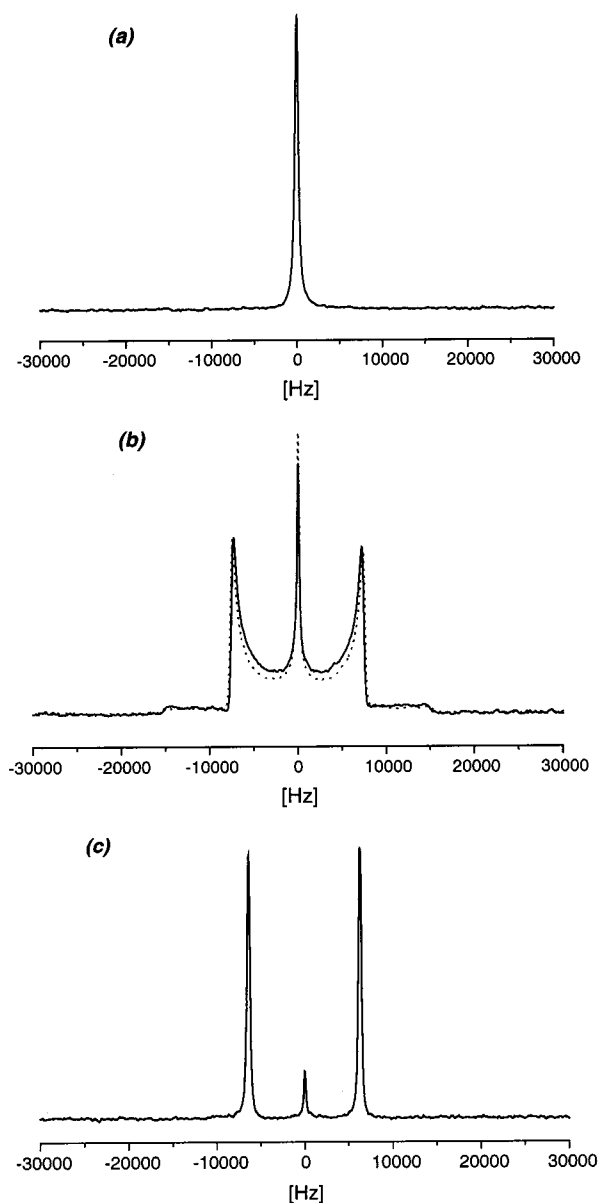


Figure 4. ^2H NMR spectrum of (a) the sponge phase (200 mM TDMAO/450 mM hexanol- d_2), (b) a randomly aligned lamellar phase (200 mM TDMAO/450 mM α -deuterated hexanol- d_2 /20 mM methylformiate) 24 h after adding methylformiate to the sponge phase and after being exposed 48 h to a magnetic field (dotted line), and (c) an aligned lamellar phase (200 mM TDMAO/450 mM α -deuterated hexanol- d_2 /20 mM methylformiate).

tion of the signals of α -deuterated hexanol- d_2 in the sponge phase and in the lamellar phase. At the end of the reaction, there still is the doublet of the aligned lamellar phase, whereas the small residual central peak is now caused by a fraction of α -deuterated hexanol- d_2 that is not bound into the bilayers of the lamellar phase but is dissolved in the aqueous phase. The possibility of D_2O formed by a deuterium-exchange process from α -deuterated hexanol- d_2 being responsible for the residual peak in Figure 5 can be safely ruled out. Because the coexistence of different phases and the transition between them can be studied, the time constant of the transformation from the sponge phase (L_3) to the lamellar phase ($L_{\alpha h}$) can be calculated. In Figure 6, the signal intensity of both the doublet and the singlet are given as a function of time after starting the reaction. The data can be fitted with a single-exponential function resulting in a common rate constant of $0.001\ \text{s}^{-1}$, which is in good

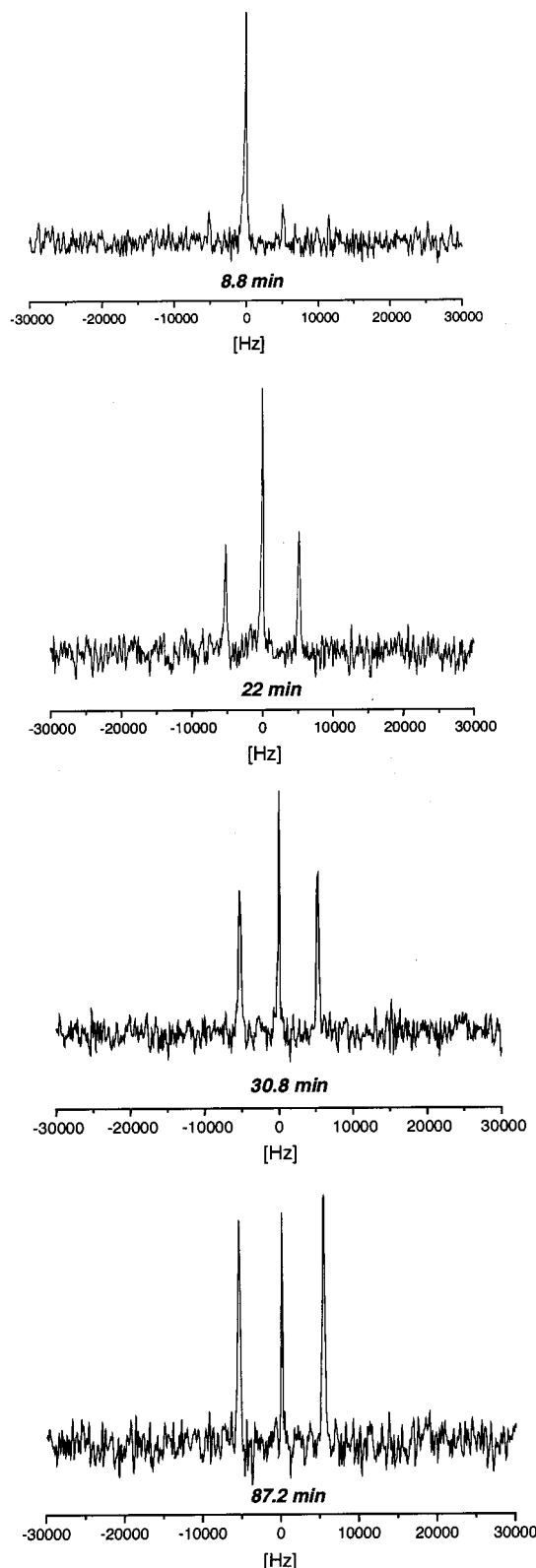


Figure 5. ^2H NMR spectra showing the transformation of the sponge phase to the lamellar phase with time (100 mM TDMAO/250 mM α -deuterated hexanol- d_2 /10 mM methylformate): from left to right, after 8.8, 22, 30.8, and 87.2 min.

agreement with the rate dependency of 0.0008 s^{-1} derived by the optical changes. We note that the NMR spectra given in Figure 5 show a small increase of the quadrupolar splitting with time. This can be attributed to aging processes, which reduce the mobility of the hexanol within the lamellar phase. This conclusion is supported by the fact that the NMR spectra of

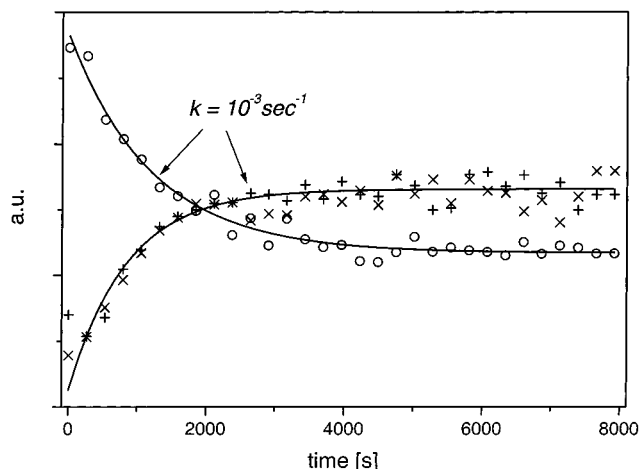


Figure 6. Signal intensity of both the doublet (cross +, x) and the singlet (circle) recorded with time.

samples with more densely packed lamellar phases show a similar increase of the quadrupolar splitting.

In addition to the experiments mentioned above (Figures 4 and 5), we prepared samples of the same system using D_2O instead of α -deuterated hexanol- d_2 . NMR measurements show a doublet without an additional central peak after completion of the transformation (Figure 7). This fact proves that all water molecules are part of the aligned aggregates though the quadrupolar splitting is much smaller as compared to that of α -deuterated hexanol- d_2 . This can be explained by more or less fast exchange processes between the lamellar aggregates and the surrounding water. But in any case, our findings prove that all water molecules are in contact with the aligned lamellar bilayers, and we are able to prepare a single-oriented lamellar phase with no additional phase present. This conclusion appears to be in contradiction to the findings of the α -deuterated hexanol- d_2 spectra (cf. Figures 4c and 5) in which clearly a central peak is observed, indicating that some α -deuterated hexanol- d_2 is dissolved in an apparently isotropic phase. For being consistent with the NMR results for D_2O , we have to assume that the central peak is actually a doublet that cannot be resolved by the NMR spectra of Figures 4c and 5. With a high-resolution NMR measurement minimizing the inhomogeneity of the magnetic field, the central signal of the oriented lamellar phase can indeed be resolved into two separated lines (Figure 8). This line separation can only occur if the dissolved α -deuterated hexanol- d_2 is affected by the anisotropic environment of the lamellar phase. Again, as in the case of the water molecules, the small separation of the two peaks indicates a fast docking process of α -deuterated hexanol- d_2 molecules to the lamellar phase. The absence of an unsplit line excludes the possibility of a coexistence of oriented and isotropic phases.

While a Pake spectrum represents the superposition of the signals of all different domain orientations, the doublet shows the uniform (i.e., complete) alignment of the crystalline domains. We note that the rotation of the NMR tube around its long axis has an influence on the quadrupolar splitting of the doublet. The specific two-dimensional Pake pattern obtained after a 90° rotation of the sample proves that the preferential orientation of the EFG of the lamellar phases in Figures 4c and 5 is perpendicular with respect to the magnetic field. Consequently, the director of the lamellar phase is also perpendicular to the magnetic field. Our conclusions about the orientation of the lamellar phase are further supported by the results of measurements of the same experiments with D_2O . In addition to that, they are in good agreement with the results of Briganti et al.¹⁴

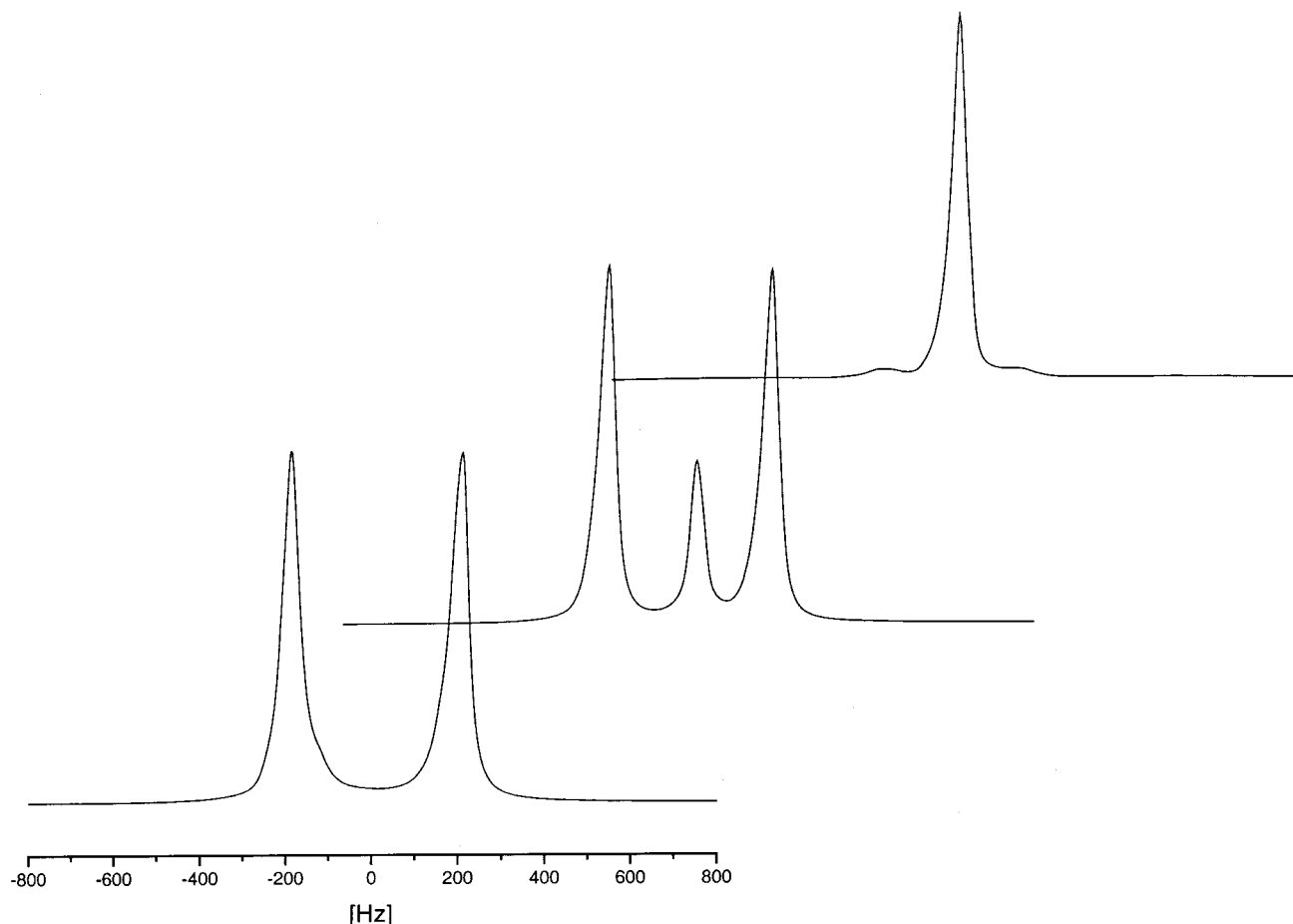


Figure 7. ^2H NMR spectra showing the transformation of the sponge phase to the lamellar phase with time using D_2O instead of α -deuterated hexanol- d_2 (900 mM TDMAO/1850 mM hexanol/90 mM methylformiate).

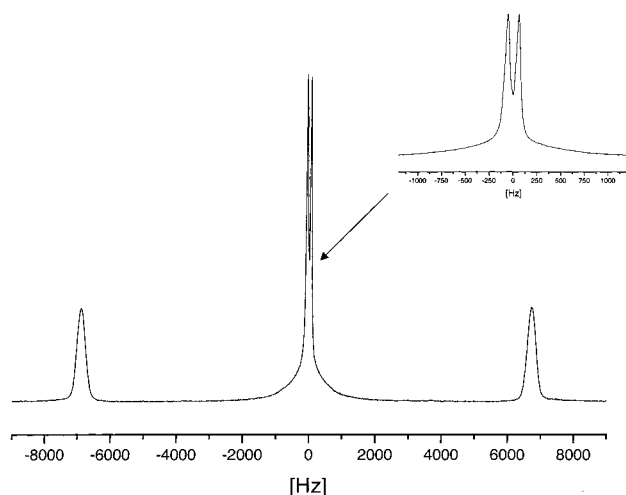


Figure 8. Line separation of the central peak of dissolved α -deuterated hexanol- d_2 in the lamellar phase.

Conclusion

The transition from the sponge phase (L_3) to the lamellar phase ($L_{\alpha\text{h}}$) of the system TDMAO/hexanol/water has been used to create macroscopically aligned systems by exploiting the special kinetic reaction with methylformiate to orient the system in a high magnetic field. The alignment process was studied by ^2H NMR spectra measurements. These measurements allow the determination of the orientation of the lamellar phase and the estimation of the time constant of the alignment process. It is further possible to control the degree of macroscopic orientation

of the system TDMAO/hexanol/water depending on the exposure time to a magnetic field.

References and Notes

- (1) Kitade, S.; Ochiai, N.; Takahashi, Y.; Noda, I.; Matsushita, Y.; Karim, A.; Nakatani, A. I.; Kim, H.; Han, C. C. *Macromolecules* **1998**, *31* (23), 8083–8090.
- (2) Abillon, Q.; Perez, E. *J. Phys. (Paris)* **1990**, *51* (22), 2543–2556.
- (3) Hertel, G.; Hoffmann, H. *Liq. Cryst.* **1989**, *5* (6), 1883–1898.
- (4) Reizlein, K.; Hoffmann, H. *Prog. Colloid Polym. Sci.* **1984**, *69*.
- (5) Rizzatti, M.; Gault, J. D. *J. Colloid Interface Sci.* **1986**, *110* (1), 258–262.
- (6) Herbst, L.; Hoffmann, H.; Kalus, J.; Reizlein, K.; Schmelzer, U. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1050–1064.
- (7) Ukleja, P.; Chidichimo, G.; Photinos, P. *Liq. Cryst.* **1991**, *9* (3), 359–367.
- (8) Weber, R.; Hoffmann, H. *Liq. Cryst.* **1987**, *3* (2), 203–216.
- (9) Bergmeier, M.; Hoffmann, H.; Thunig, C. *J. Chem. Phys.* **1997**, *110* (30), 5567–5571.
- (10) Hoffmann, H.; Thunig, C.; Valiente, M. *Colloids Surf.* **1992**, *67*, 223–237.
- (11) Hoffmann, H.; Thunig, C.; Munkert, U.; Meyer, H. W.; Richter, W. *Langmuir* **1992**, *8* (11), 2629–2638.
- (12) Hoffmann, H.; Thunig, C.; Schmiedel, P.; Munkert, U. *Langmuir* **1994**, *10*, 3972–3981.
- (13) Bergmeier, M.; Gradzielski, M.; Thunig, C.; Hoffmann, H. *Nuovo Cimento Soc. Ital. Fis., D* **1998**, *20*, 2251–2264.
- (14) Briganti, G.; Segre, A. L.; Capitani, D.; Casieri, C.; La Mesa, C. *J. Phys. Chem.* **1999**, *103*, 825–830.
- (15) Svärd, M.; Schurtenberger, P.; Fontell, K.; Jönsson, B.; Lindman, B. *J. Phys. Chem.* **1988**, *92*, 2261–2270.
- (16) Capitani, D.; Casieri, C.; Briganti, G.; La Mesa, C.; Segre, A. L. *J. Phys. Chem.* **1999**, *103*, 6088–6095.
- (17) Firouzi, A.; Schaefer, D. J.; Tolbert, S. H.; Stucky, G. D.; Chmelka, B. F. *J. Chem. Phys.* **1997**, *119*, 9466–9477.
- (18) Ekwall, P. In *Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic Press: New York, 1975.