Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Homogeneous and Inhomogeneous Director Dynamics of a Fluorinated Liquid Crystal

Michael Bender [a], Peter Holstein [a] & Dieter Geschke [a]

[a] Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstraße 5, 04103, Leipzig, Germany

Version of record first published: 24 Sep 2006

To cite this article: Michael Bender, Peter Holstein & Dieter Geschke (2001): Homogeneous and Inhomogeneous Director Dynamics of a Fluorinated Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 363:1, 85-95

To link to this article: http://dx.doi.org/10.1080/10587250108025260

Mol. Cryst. Liq. Cryst., Vol. 363, pp. 85-95
Reprints available directly from the publisher
Photocopying permitted by license only

Homogeneous and Inhomogeneous Director Dynamics of a Fluorinated Liquid Crystal

MICHAEL BENDER*, PETER HOLSTEIN and DIETER GESCHKE

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstraße 5, 04103 Leipzig, Germany

(Received September 21, 2000)

The director reorientation of a thermotropic nematic liquid crystal in electric and magnetic fields has been investigated by means of ^{1}H and ^{19}F nuclear magnetic resonance. A new method which uses electric fields to set the desired initial angle of the nematic director with respect to the magnetic field is described. Using this method it was possible to perform reorientation experiments in the magnetic field starting in a large number of initial angles and to investigate the transition from homogeneous to inhomogeneous reorientation processes in detail. It is shown that reorientation processes in the presence of both electric and magnetic fields remain homogeneous for initial angles close to 90°. An analysis of the ^{1}H and ^{19}F NMR spectra shows inhomogeneous processes in the magnetic field beginning at considerably smaller angles. An intermediate region of about 6° where homogeneous and inhomogeneous processes take place at the same time has been found.

Keywords: inhomogeneous dynamic processes; electric fields; fluorinated liquid crystal; nuclear magnetic resonance

1 INTRODUCTION

The director reorientation of nematic liquid crystals (LCs) depends strongly on the initial angle between the director and the external field. From theoretical predictions [1, 2] a qualitatively different relaxation behaviour can be expected for initial angles $\varphi_0 < 45°$ and $\varphi_0 > 45°$, where the critical angle $\varphi_c = 45°$ is a typical threshold to distinguish homogeneous from inhomogeneous processes. In the first case a uniform director distribution can be assumed and the Ericksen-Leslie theory [3] describes the reorientation process very well. The latter case is represented by a director distribution which changes during the reorientation process.

* Author to whom correspondence should be addressed: Tel.: +49-341-97-32573; fax: +49-341-97-32497; e-mail: bender@physik.uni-leipzig.de

A lot of nuclear magnetic resonance (NMR) results dealing with liquid crystalline polymers have been published [1, 2, 4–10] but due to the difficulty to change the director orientation data about low molar mass LCs are scarce [11–14]. While a critical angle close to 45° can be found in most LCPs this value is much higher for low molar mass LCs (≥ 70°). In this work we investigate the transition from homogeneous to inhomogeneous flow in a fluorinated low molar mass LC by observing a large number of reorientation processes with initial angles near the critical angle. The NMR experiments have been carried out using a recently developed method [15–17] where pulsed electric fields have been used in addition to the static magnetic field of the NMR spectrometer to induce dynamic processes in the LC. Time resolved ^{1}H NMR experiments with a resolution in the order of 10 μs yield spectra which represent different orientational states of the LC during the reorientation process. These experiments have been extended to ^{19}F NMR investigations which have the advantage of a large chemical shift anisotropy. The high sensitivity of ^{19}F NMR compared to ^{13}C and ^{2}H NMR is a further advantage because thin LC cells have been used. Angle dependent ^{19}F NMR spectra of oriented systems provide therefore information about local order and dynamics without the need of ^{1}H decoupling or magic angle spinning [18]. The spectra of partially fluorinated LCs represent therefore specific molecular sites and are a complementary approach to ^{2}H NMR which has extensively been used to investigate various director distributions [7–9]. An analysis of the time and angle dependent ^{1}H and ^{19}F NMR lineshape provides the critical angle and information about the transition process.

2 THEORETICAL

A nematic liquid crystal well aligned in the strong magnetic field of a NMR spectrometer can be described by a director field $\boldsymbol{n}(\boldsymbol{r})$ which is homogeneous in space ($\nabla \boldsymbol{n} = 0$). In homogeneous dynamic processes the condition $\nabla \boldsymbol{n} = 0$ holds true while the angle between the director $\boldsymbol{n}$ and the magnetic field $\boldsymbol{B}_0$ changes. Such processes can be understood in terms of a simplified form of the Leslie-equation with the well known solution [3, 17]

$$\varphi(t) = \arctan\left\{\tan(\varphi_0 - \varphi_{es}) \cdot \exp\left(-\frac{t}{\tau}\right)\right\} + \varphi_{es}, \qquad (1)$$

where φ is the angle between the nematic director $\boldsymbol{n}$ and the magnetic field $\boldsymbol{B}_0$, φ_0 is the initial angle $\varphi(t = 0)$, φ_{es} is the equilibrium established for $t \to \infty$ and τ is the time constant describing the process.

Dynamic processes in the magnetic field start in an initial angle φ_0 and relax back to the equilibrium $\varphi_{es} = 0°$. Processes taking place in the presence of both electric and magnetic fields start in the equilibrium defined by the magnetic field ($\varphi_0 = 0$, $E = 0$) and evolve into the equilibrium established by both fields (φ_{es}, $E > 0$). For strong electric fields the director aligns nearly parallel to the electric field and φ_{es} is only slightly less than the angle α between both fields.

In the pure magnetic case ($E = 0$) the time constant τ is given by

$$\tau = \frac{\mu_0 \gamma_1}{\Delta\chi B^2}, \tag{2}$$

where μ_0 is the permeability of free space, γ_1 is the rotational viscosity and $\Delta\chi$ is the diamagnetic anisotropy. In presence of an additional electric field τ is a more complicated function of $\boldsymbol{E}$, $\boldsymbol{B}_0$, $\Delta\varepsilon$, $\Delta\chi$ and α [17].

The critical angle φ_c separates the region of homogeneous dynamics ($\varphi_0 < \varphi_c$) from the region $\varphi_0 > \varphi_c$ where the dynamics behaves more complicated and cannot be described by equ. 1. Inhomogeneous processes are characterized by a director field $\boldsymbol{n}(\boldsymbol{r})$ with $\nabla \boldsymbol{n} \neq 0$ and a director distribution which changes during the reorientation process.

The reorientation process can be investigated by acquiring NMR spectra at different states of the process. In case of a homogeneous director reorientation it is possible to obtain the angle between the director and the magnetic field by analyzing the line width or line position. The dipolar splitting of a pair of homonuclear spins in a nematic liquid crystal is given by

$$\Delta\nu = \frac{3\mu_0\gamma^2\hbar}{8\pi\langle r_{ij}^3\rangle} \cdot \left\{\frac{1}{2}(3\cos^2\varphi - 1)\right\} \cdot S, \tag{3}$$

where γ is the gyromagnetic ratio of protons, $\hbar$ is Planck's constant divided by 2π, S is the order parameter and $\langle r_{ij}\rangle$ is the mean distance between adjacent resonating nuclei. As the dipolar broadened ^{1}H NMR spectrum is a superposition of a large number of such doublets the line width is under certain conditions [19] proportional to equ. 3 and φ can be calculated from $\Delta\nu$.

While the chemical shift can be neglected in ^{1}H NMR spectra at low fields it has the same order of magnitude as the dipolar interaction in ^{19}F NMR spectra. ^{19}F NMR spectra of LCs with a small number of ^{19}F nuclei consist therefore of a few well resolved lines with a superimposed dipolar broadening or splitting of some kHz. The position of each line changes according to equ. 4 and due to the large chemical shift anisotropy the angle φ can be obtained from the line position with high precision. The angle dependent chemical shift $\delta(\varphi)$ varies according to

$$\delta(\varphi) = \delta_{iso} + \frac{1}{2} \cdot (3\cos^2\varphi - 1)(\delta_0 - \delta_{iso}) \tag{4}$$

where δ_{iso} is the isotropic chemical shift and δ_0 is the nematic chemical shift at $\boldsymbol{n} \parallel \boldsymbol{B}_0$.

In case of an inhomogeneous reorientation the line shape changes not only due to the time dependent angle between the director and the magnetic field but also due to the director distribution. A detailed analysis of the director distribution based on ^{1}H NMR spectra has been done by Martins et. al. [1, 2], Spiess et. al. published similar ^{2}H results [7–9].

3 EXPERIMENTAL

A fluorinated form (Figure 1) of a 4,4′-disubstituted biphenyl cyclohexane (BCH-5 F.F.F., Merck) has been investigated by means of ^{1}H and ^{19}F NMR. The diamagnetic anisotropy $\Delta\chi$ as well as the dielectric anisotropy $\Delta\varepsilon$ of BCH-5 FFF is positive and the director aligns parallel to the external field. The liquid crystal has been filled in a 500 μm capacitor cell which is connected to a laboratory made high voltage supply. High voltage pulses of different shape, voltage and duration can be produced by this setup and are driven by the NMR pulse program. With this experimental setup it is possible to investigate different static and dynamic orientational processes by means of NMR [17]. A 100 MHz spectrometer (Bruker MSL100) has been used because of its comparatively low magnetic field of 2.35 T. Higher magnetic fields would require high voltages above 500 V to overcome the torque of the magnetic field acting on the director. The spectrometer is equipped with a laboratory built ^{1}H/^{19}F NMR probe with special high voltage connections for reduced radio frequency noise [16] and a goniometer. The latter is essential for any quantitative data analysis because the electric torque depends on the angle α between the electric and magnetic field and has to be set carefully. Electric pulses of constant voltage but increasing duration have been used to investigate the director reorientation in the electric field and to set initial angles between the director and the magnetic field. The reorientation in the magnetic field starting in different electrically set angles has been investigated to find the critical angle.

Short electric pulses have been used to avoid electrical currents inside the cell which often occur in static electric fields. Most LCs contain impurities or charge carriers which can lead to turbulent flow inside the cell. The director field caused by this flow would overlap with the dynamic processes described above and it would be difficult to distinguish both processes. The switching processes in the electric field have therefore been checked with optical methods and it turned out that electric pulses with a duration of a few hundred milliseconds do not cause electric turbulence as long as the voltage does not exceed several hundred volt and the delay between the pulses is longer than the duration of the pulse, e.g. 100 ms and 1 s.

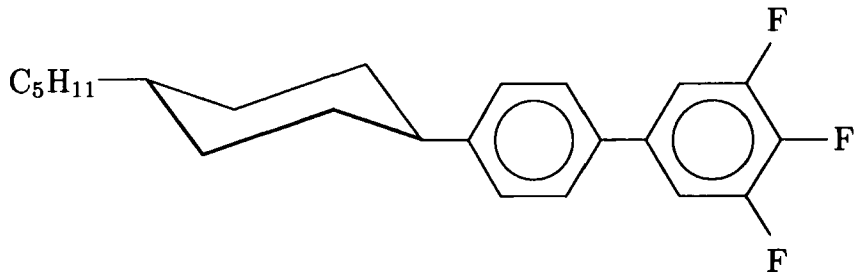

FIGURE 1 Thermotropic nematic liquid crystal BCH-5 FFF, $T_{C\text{-}N} = 25.0°C$, $T_{N\text{-}I} = 54.8°C$, $\Delta\varepsilon$, $\Delta\chi > 0$

While equ. 1 is strictly valid only in the homogeneous case inhomogeneous processes with an effective viscosity $\gamma_{eff} \leq \gamma_1$ which is only slightly less than the rotational viscosity γ_1 also give acceptable fits to equ. 1. This behaviour is typical for some low molar mass LCs [11] and measured $\varphi(t)$ data cannot be used to identify homogeneous processes. On the other hand processes which cannot be described by equ. 1 are certainly inhomogeneous.

Homogeneous processes are therefore identified by comparison of the NMR lineshape. The electric field can be used to establish an equilibrium in any angle φ between 0° and $\alpha < 90°$ [17]. NMR spectra can be taken in different angles in respect to $\boldsymbol{B}_0$ with the director statically aligned in this direction. Using these spectra and especially the spectrum in the magic angle (54.7°) as a reference for a homogeneous director distribution it is possible to distinguish spectra taken during a homogeneous process from spectra taken in a inhomogeneous one. By variation of the initial angle φ_0 the critical angle φ_c can be obtained.

As can be expected from Figure 1 the isotropic ^{19}F NMR spectrum consists of two lines with intensities in a ratio of 2:1. In the nematic phase the line of the two magnetically equivalent ^{19}F nuclei splits in the dipolar field of the adjacent protons and gives a doublet as indicated in Figure 3 (left). The dipolar splitting can be demonstrated by comparing ^{19}F NMR spectra taken with and without ^{1}H decoupling (Figure 3, insert). ^{1}H decoupling removes the heteronuclear dipolar interaction [20] and the doublet changes into one line. The reorientation experiments have been carried out without decoupling and consist therefore of three lines which can be analyzed independently using equ. 4. A further method to describe the reorientation is the dipolar splitting from the heteronuclear interaction using equ. 3.

All ^{19}F chemical shifts have been referenced relative to $CFCl_3$ ($\delta = 0$ ppm). The ^{19}F NMR data are given in Hertz because the chemical shift anisotropy and

dipolar effects have to be discussed. The experiments have been carried out at 94.3 MHz ^{19}F frequency and 10000 Hz correspond to 106.1 ppm.

3.1 Dynamics in the electric field

Dynamic processes in the presence of both electric and magnetic fields stay homogeneous even up to angles $\varphi_0 \lesssim 88°$. The spectra shown in Figure 2 (^1H) and Figure 3 (^{19}F) have been taken with 237 V pulses on a 500 μm cell and $\alpha = 84.4°$. Comparison of the ^1H NMR spectra in the magic angle (Figure 2, insert) with a static ^1H NMR spectrum does not show any line broadening due to the director dynamics. The ^{19}F NMR spectra are also well resolved and nearly identical to static spectra taken in the same angles. The line width (^1H, Figure 2) and the line position (^{19}F, Figure 3) can be very well fitted to equ. 1 by replacing φ in equ. 3 and equ. 4. The results from the ^1H and ^{19}F NMR data are identical within the experimental error: The time constant $\tau_H = 10.5$ ms obtained from the ^1H NMR spectra is very close to $\tau_{F1} = 10.3$ ms obtained from the ^{19}F line calculated from the two dipolar split lines. A fit to the dipolar splitting yields $\tau_D = 10.4$ ms. The result $\tau_{F2} = 10.9$ ms of the ^{19}F line starting at ~ 11800 Hz is less accurate due to the overlap of two lines.

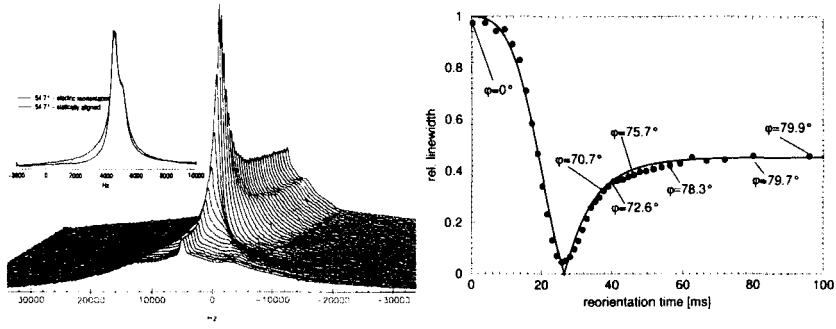

FIGURE 2 BCH-5 FFF, 42°C, ^1H NMR data – homogeneous reorientation in the electric field. ^1H NMR spectra (left) taken after 237 V pulses of increasing length (0 ms ... 150 ms) and the relative line width as a function of the reorientation time (right). A fit of equ. 1 and equ. 3 gives $\tau = 10.6$ ms. The 54.7° spectrum (left, insert, solid line) taken during the reorientation has nearly the same lineshape as a spectrum with the director statically aligned in the magic angle (dashed line)

The electrically driven reorientation process is therefore homogeneous for angles φ_0 at least up to 84.4° and can be used to set the initial angles which are required for the investigation of reorientation processes in the magnetic field. The angles given in Figure 2 (right) have been calculated with equ. 1 and

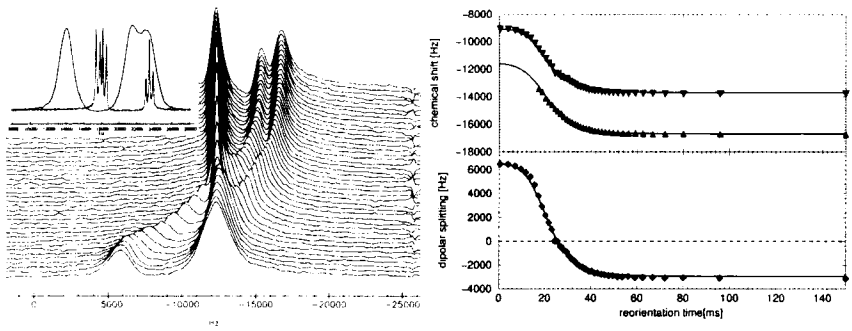

FIGURE 3 BCH-5 FFF, 42°C, ^{19}F NMR data – homogeneous reorientation under exactly the same conditions as in Figure 2. The ^{19}F NMR spectra (left) can be analyzed using equ. 1 and equ. 4. The results (right) are $\tau_1 = 10.3$ ms, $\tau_2 = 10.9$ ms and $\tau_D = 10.4$. The line position (▼) and the dipolar splitting (♦) of the first line has been calculated from two lines at the left side of the plot. The insert (left) shows the spectrum at $\varphi = 0$ with (dashed line) and without (solid line) ^1H decoupling

$\tau_H = 10.5$ ms for different reorientation times. Electric pulses with a duration of $t_E = 37.7$ ms ... 150 ms corresponding to angles $\varphi = 70.6°$ ... 79.9° have been used to set the initial angles for the reorientation experiments in the magnetic field which are described below.

3.2 Dynamics in the magnetic field

Homogeneous reorientation processes in the electric field have been used to turn the director into different angles in respect to $\boldsymbol{B}_0$. The reorientation process in the magnetic field starting in these angles can easily be investigated. As the electrical switching can be done automatically by changing the duration of the electric pulses applied to the LC cell it is possible to study magnetic reorientation processes starting in a large number of different initial angles φ_0 in a short time. 20 experiments with $63° \leq \varphi_0 \leq 79.9°$ have been done using 237 V pulses with a duration between 33 ms and 150 ms. As an example the spectra of a homogeneous reorientation process in the magnetic field starting in an initial angle $\varphi_0 = 70.6°$ are shown in Figure 4 (^1H) and Figure 5 (^{19}F).

The data analysis can be carried out in the same way as in the electric case and leads to a time constant $\tau_H = 14.2$ ms (^1H) and $\tau_{F1} = 13.9$ ms (^{19}F). The dipolar splitting gives $\tau_D = 13.7$ ms. The analysis of the second line is again less reliable and gives $\tau_{F2} = 15.1$ ms. An inhomogeneous process is shown in Figure 6 (^1H) and Figure 7 (^{19}F). While the ^1H NMR spectra do not much differ from Figure 4 the linewidth changes in a way which cannot be described by equ. 1. The poor fit

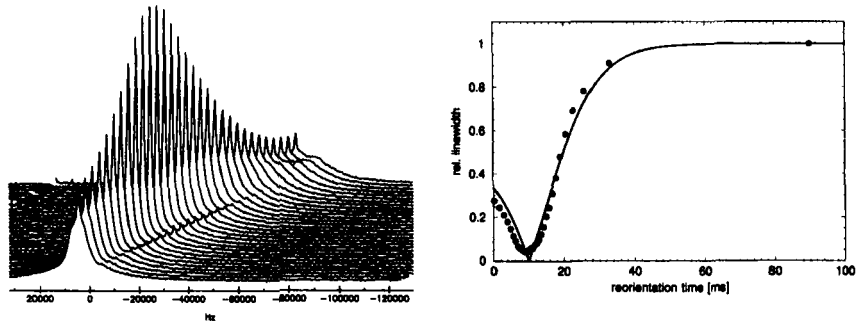

FIGURE 4 BCH-5 FFF, 42°C, ^{1}H NMR data – homogeneous reorientation in the magnetic field starting at an initial angle $\varphi_0 = 70.6°$. The ^{1}H NMR spectra (left) have been taken taken 0 ms ... 130 ms after a 237 V, 37.7 ms pulse. A fit of the linewidth (right) using equ. 1 and equ. 3 with $\varphi_{es} = 0$ gives $\tau = 14.3$ ms

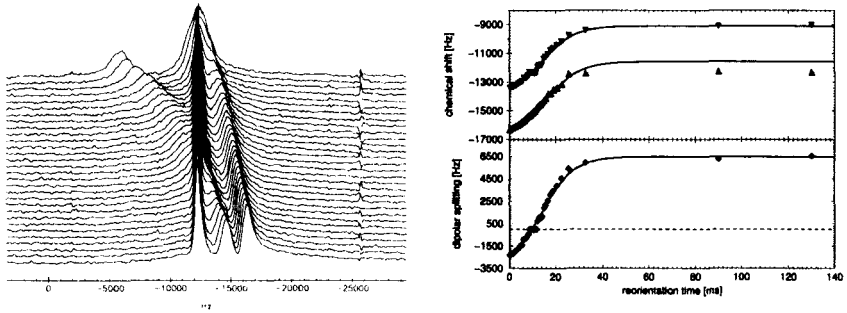

FIGURE 5 BCH-5 FFF, 42°C, ^{19}F NMR data – homogeneous reorientation under exactly the same conditions as in Figure 4. The ^{19}F NMR spectra (left) can be analyzed using equ. 1 and equ. 4. The results (right) are $\tau_1 = 13.9$ ms, $\tau_2 = 15.1$ ms and $\tau_D = 13.7$ ms. The line position (▼) and the dipolar splitting (♦) has been analyzed as in the electric case

in Figure 6 (right) also shows that the introduction of a constant effective viscosity $\gamma_{eff} \neq \gamma_1$ does not solve the problem. An angle dependent viscosity $\gamma_{eff}(\varphi)$ would be required [1] which leads to a somewhat smaller viscosity $\gamma_{eff} < \gamma_1$ at the beginning of the process and to larger values $\gamma_{eff} > \gamma_1$ at the end. The constitutive director distribution has a much more impressive effect on the ^{19}F NMR spectra. The lines decompose at their initial positions and reappear near their equilibrium positions with no well resolved peaks in between (Figure 7).

It seems that the sharp ^{19}F line at ~ 12000 Hz behaves in a different way but this is not the case. According to equ. 4 the line position can only vary in a range given by $\delta_0 - \delta_{iso}$. With $\delta_0 \approx -12378$ Hz and $\delta_{iso} = -12266$ Hz the position is

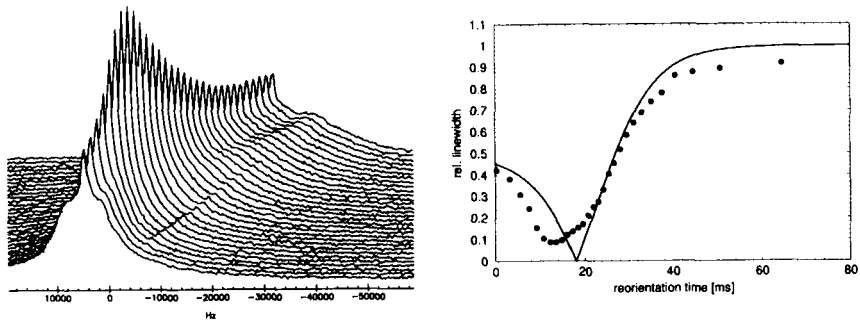

FIGURE 6 BCH-5 FFF, 42° C, ^{1}H NMR data – inhomogeneous reorientation in the magnetic field starting at an initial angle $\varphi_0 = 79.9°$. The ^{1}H NMR spectra (left) have been taken taken 0 ms ... 65 ms after a 150 ms, 237 V pulse. The fit has been performed in the same way as in Figure 4 but cannot describe the data ($\tau = 13.0$ ms)

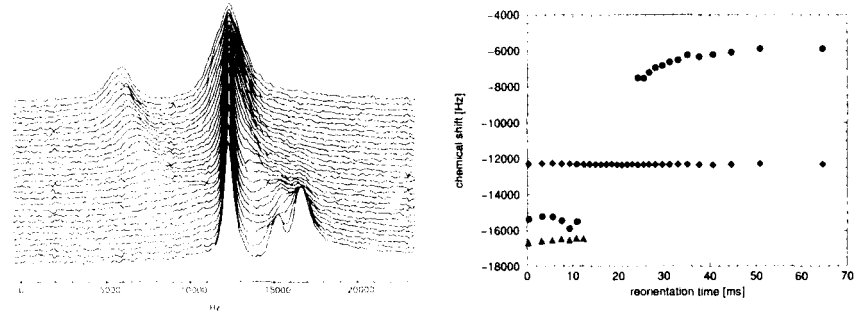

FIGURE 7 BCH-5 FFF, 42°C, ^{19}F NMR data – inhomogeneous reorientation under exactly the same conditions as in Figure 6. A fit according to equ. 1 is not possible

limited to a range of a few hundred Hz. As the director distribution is also limited to this range the line remains nearly unaffected while the two other lines broaden by a factor of ~ 10.

Between the two processes which are definitely homogeneous and inhomogeneous the behaviour changes continously showing attributes of both types at the same time. It is therefore difficult to define the critical angle for such a complex behaviour. An analysis of the ^{1}H NMR lineshape in the magic angle is shown in Figure 8. In the magic angle (54.7°) the dipolar interaction is nearly averaged out (equ. 3) and the line broadening due to the director distribution can easily be identified. The lineshape of homogeneous processes can be compared with the lineshape found in different inhomogeneous processes (Figure 8, insert). The

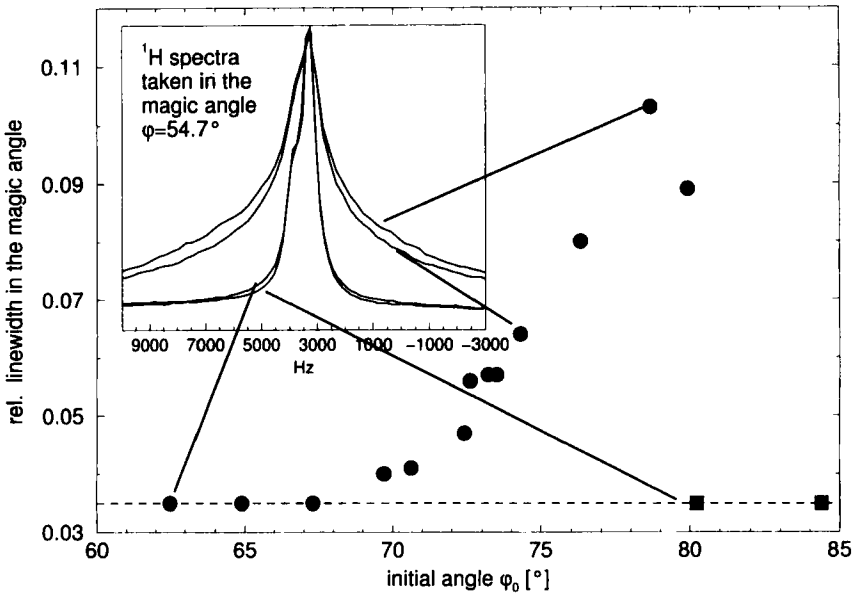

FIGURE 8 BCH-5 FFF, 42°C, ^{1}H NMR data – minimal linewidth of the ^{1}H NMR spectra as a function of the initial angle φ_0. In the magnetic case (•) the line width increases above the critical angle. In the electric case (■) the critical angle is greater than 85° and the line width stays constant for $\varphi_0 <$ 85°

linewidth of homogeneous processes in the electric and in the magnetic field as well is constant and independent of the initial angle. Beginning at an angle of $\varphi_0 \approx 68°$ the linewidth increases indicating the beginning of inhomogeneous processes. The quality of the fits also decreases but the first noticeable effect appears at a larger angle of about $\varphi_0 \approx 74°$. Observation of the ^{19}F NMR spectra and the analysis of the line position also supports the higher value of $\varphi_0 \approx 74°$ but it is difficult to find a parameter which can be plotted as a function of the initial angle φ_0.

4 CONCLUSION

It has been shown that reorientation processes in simultaneously present electric and magnetic fields stay homogeneous for initial angles up to 85°. The reorientation in magnetic field turns from homogeneous to inhomogeneous at a critical angle $\varphi_c = 74°$ with a preceeding intermediate region of about 6° where proc-

esses of both type seem to overlay. Reorientation experiments using an electric field to establish initial angles for dynamic processes in the magnetic field of the NMR spectrometer have proved its worth as an powerful tool for fast and precise φ_c measurements of low molar mass LCs. Exployting the thorough reversible reorientation processes in nematic LCs it is possible to collect a large number of data and to run different experiments with the same setup. Since the critical angle φ_c^{E} in the electric field is larger than the critical angle φ_c^{B} in the magnetic field the second field must have a stabilizing effect on the reorientation process.

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) and the Deutsche Akademische Austauschdienst (DAAD) are acknowledged for financial support (HO 1619/5–1,3) and E. Merck, Darmstadt (Germany) for providing the liquid crystals. We also want to thank Prof. Dr. R. K. Harris, University of Durham, United Kingdom, for the opportunity to use his spectrometer for some of the ^{19}F NMR experiments and for helpful discussions.

References

[1] A. F. Martins, P. Esnault, and F. Volino, Phys. Rev. Lett. **57**, 1745 (1986).
[2] P. Esnault, J. P. Casquilho, F. Volino, A. F. Martins, and A. Blumstein, Liquid Crystals **7**, 607 (1990).
[3] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon, Oxford, second edition, 1993.
[4] J. P. Casquilho, P. Esnault, F. Volino, M. Mauzac, and H. Richard, Mol. Cryst. Liq. Cryst. **180B**, 343 (1990).
[5] L. N. Gonçalves, J. P. Casquilho, J. Figueirinhas, C. Cruz, and A. F. Martins, Liquid Crystals **14**, 1485 (1993).
[6] J. S. Moore and S. I. Stupp, Macromolecules **20**, 282 (1987).
[7] D. van der Putten, N. Schwenk, and H. W. Spiess, Liquid Crystals **4**, 341 (1989).
[8] N. Schwenk, C. Boeffel, and H. W. Spiess, Liquid Crystals **12**, 735 (1992).
[9] N. Schwenk and H. W. Spiess, J. Phys. II, France **3**, 865 (1993).
[10] P. Holstein, E. B. Barmatov, D. Geschke, M. Bender, and V. P. Shibaev, Colloid Polym. Sci. **278**, 711 (2000).
[11] H. Gotzig, S. Grunenberg-Hassanein, and F. Noack, Z. Naturforsch. **49a**, 1179 (1994).
[12] M. L. Magnuson and B. M. Fung, J. Chem. Phys. **100**, 1470 (1994).
[13] M. L. Magnuson and B. M. Fung, Liquid Crystals **20**, 293 (1996).
[14] E. Ciampi et al., J. Chem. Phys. **107**, 5907 (1997).
[15] P. Holstein, A. C. D. Lopes, J. Rauchfuß, and D. Geschke, Magn. Reson. Chem. **35**, 420 (1997).
[16] P. Holstein, J. Rauchfuß, M. Winkler, G. Klotzsche, and D. Geschke, Solid State NMR **10**, 225 (1998).
[17] M. Bender, P. Holstein, and D. Geschke, J. Chem. Phys. **113**, 2430 (2000).
[18] S. L. Grage and A. S. Ulrich, J. Magn. Reson. **146**, 81 (2000).
[19] H. Schmiedel, B. Hillner, S. Grande, A. Lösche, and S. Limmer, J. Magn. Reson. **40**, 369 (1980).
[20] R. K. Harris and P. Jackson, Chem. Rev. **91**, 1427 (1991).