Macromol. Symp. ***184,*** *137–152 (2002)*

Application of Electric Fields in NMR

Peter Holstein[1], *Michael Bender*[2]

[1] Sinus Messtechnik GmbH Leipzig, D-04347 Leipzig, Föpplstr. 13, Germany
[2] Universität Leipzig, Fakultät für Physik und Geowissenschaften, D-04103 Leipzig; Linnéstr. 5, Germany

Summary: Anisotropic orientation states in materials such as liquid crystals, liquid crystalline polymers or polymeric electrets can be induced by the application of electric fields. This behaviour is exploited extensively in displays or sensors. Anisotropic optical properties induced by relatively high electric field strengths are used in the well known displays made from liquid crystalline materials. The anisotropy of electric properties in polymeric materials gives rise to properties such as the high piezoelectricity of fluorine containing electrets. Attempts have been made to investigate the orientational state induced by electric fields after poling using NMR techniques. However, there is only access to the irreversible part of the electrically induced orientation. *In-situ* application of (high) voltages during NMR experiments enables the investigation of the influence of the electric field on molecular orientational states or electrically-induced morphological changes. The NMR methods have been modified to investigate the dynamics of reorientation processes in electric fields and to extend the possible time range towards below1ms. The application of high voltages in NMR experiments requires experimental specifications. Some of our experiences are outlined in this paper.

Introduction

It is well known that organic materials and polymers can change their properties when exposed to external electrical fields. Many technical applications are based on the modification of material properties by means of electric fields. Voltage application can produce either irreversible or reversible effects. Examples are electrically prepared polymer electrets and the use of liquid crystals in displays. Aim of this contribution is the discussion of the potential of the use of an additional electric field in NMR experiments. The main emphasis will be on new methods for the observation of reorientation processes induced by switched electrical fields. Solid-state NMR techniques have been modified in order to investigate dynamic molecular effects (e.g. molecular reorientations) due to simultaneously applied external electric fields on electrically sensitive materials such as liquid crystals (LC), liquid crystalline polymers (LCP) [1 , 2, 3] and polymeric electrets [4]. The NMR samples are capacitor cells. The

CCC 1022-1360/00/$ 17.50+.50/0

use of relatively thin systems (10 - 200 μm) provides a poor signal-to-noise-ratio. Additionally, there are demanding technical problems due to the electrical voltage application. The key to achieve a reasonable signal intensity is the modification of the NMR experiment exploiting the reversibility of orientational processes in external fields.

With a capacitor placed in the rf-coil of an NMR-spectrometer it is possible to investigate reorientational processes in liquid crystalline polymers induced by the static magnetic field of the spectrometer and the dynamic electric field between the capacitor plates. The director can be rotated in every desired angle by the simultaneous application of the electric field as a result of the competing magnetic and electric torques which are caused by anisotropic material properties. Molecular reorientation processes with a time resolution down to 5 μs were observed.

The dynamics of the process depends strongly on the strength of the electric field (and of the magnetic field) and on the temperature. The arrangement allows the *in situ* measurement of switching times, of the viscosity γ_1, of order parameters etc.

In a series of papers, the methodological development and applications of the use of electrical fields in NMR experiments have been reported [1-6, 7, 8]. An overview of the NMR methodology applied on liquid crystalline systems is given by Dong [9]

Theoretical

Typically, the NMR Hamiltonian can be written as a superposition of some contributions. Examples for the application of electric fields have been given for various NMR interactions which are summarized in equ. 1

$$H = H_{\mathrm{Z}} + H_{\mathrm{D}} + H_{\mathrm{CS}} + H_{\mathrm{Q}} + H_{\mathrm{RF}} \qquad (1)$$

where H_z denotes the Zeeman interaction, H_D the dipolar interaction (homonuclear and heteronuclear), H_{CS} the chemical shift, H_Q the quadrupolar interaction and H_{RF} the interaction with the radio frequency pulse. These interactions are, except the Zeeman interaction, asymmetric. The extent of the effects for the different interactions varies with the nuclei. The asymmetry is the source of information which can be obtained by the experiments discussed in the paper. In some cases, one type of interaction dominates (the homonuclear dipolar interaction for protons, the quadrupolar interaction for deuterated materials). A superposition of homonuclear and heteronuclear interaction, isotropic and anisotropic chemical shift must be taken into consideration for the fluorinated substances where all contributions are of similar order which complicates the interpretation. On the other hand, using the versatility of the NMR pulse experiments, this situation is a source of interesting information [5].

Some formulae are given which illustrate the situation for molecules which rotate (fast) around a prefered axis which provides some very useful simplifications. The orientation, e.g. as a consequence of anisotropic magnetic material properties, provides a macroscopic average alignment of the molecular axes (the so-called director with the angle φ relatively to B_0). Typical systems are liquid crystals and liquid crystalline polymers in their nematic phase. S is the order parameter which is here only given as a general product. Then, the line splitting $\Delta\nu$ due to the dipolar interaction of the homonuclear spins depends on the relative orientation of the director with respect to the magnetic field:

$$\Delta\nu = \frac{\mu_0}{4\pi}\left(\frac{\gamma}{2\pi}\right)^2 \frac{3h}{\langle r_{ij}^3\rangle}\left(\frac{3}{2}\cos^2\varphi - \frac{1}{2}\right)\cdot S \qquad (2)$$

γ is the gyromagnetic ratio, h is Planck's constant , $\langle r_{ij}\rangle$ denotes the mean distance between resonating nuclei . The angle φ can be calculated from $\Delta\nu$. Analogously, for the quadrupolar interaction (^{2}H NMR) a similar expression can be obtained:

$$\Delta\nu_Q = \frac{3}{4}\frac{e^2qQ}{h}\left(3\cos^2\varphi - 1\right)\cdot S \qquad (3)$$

where q denotes the electric field gradient, Q the quadrupole moment and e the elementary charge. Chemical shift effects can be discussed by the following equation

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

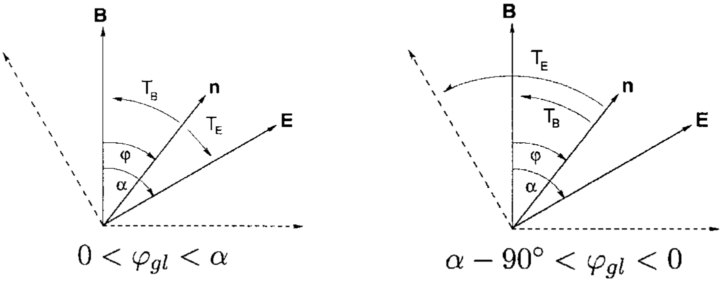
δ_{iso} is the isotropic chemical shift. φ has the same meaning as in equ. (2,3). δ_0 denotes the chemical shift for the parallel orientation of the director in the nematic phase. It can be complicate to obtain the isotropic value of the chemical shift for anisotropic systems. The electric field application is a possible approach to map a complete angular dependence in such cases where the spontaneous orientation caused by the field of an NMR-spectrometer would prevent the access to other anisotropy values. The anisotropy of the chemical shift compared to the dipolar interaction can be neglected for protons in lower magnetic fields (predominantly used for these studies (2.4 T)). However, even in that case the anisotropic chemical shift effects predicted by equ. (4) can be observed on static samples for protons when narrowing techniques (multiple pulse) are applied in order to remove the homonuclear dipolar interaction. Narrowing factors up to 300 could be achieved which enabled the investigation of the ^{1}H NMR chemical shift anisotropy induced by an electric field on a contacted sample [6].

The angle φ can be distributed around a preferred direction (static) or by inhomogeneity (transient) effects during the reorientation process. In that case the molecular distributions must be considered [10, 11] in order to use equations (2) –(4).

The orientation of liquid crystals and liquid crystalline polymers in external fields depends on their anisotropic material properties and the strength of the fields. The torques which act in an electric and magnetic field on the director n can be written as

$$T_e = \frac{\varepsilon_0}{2}\Delta\varepsilon E^2 \sin(2\theta_e) \quad (5) \quad \text{and} \quad T_m = \frac{\Delta\chi}{2\mu_0} B^2 \sin(2\theta_m) \quad (6)$$

T_{el} and T_m are the torques in the electric and magnetic field. $\Delta\varepsilon$ and $\Delta\chi$ are the dielectric and diamagnetic anisotropy. θ is the angle between the field (electric field E or magnetic field B) and the director of the sample. μ_0 and ε_0 are the usual natural constants of the permeability and permittivity of the vacuum. The physical situation is more complicate when competing fields occur which is the case in the NMR experiments with electric fields. Some different situations can be distinguished (e.g. $\Delta\varepsilon$ and $\Delta\chi$ are positive, Figure 1 *left,* $\Delta\varepsilon$ is negative and $\Delta\chi$ is positive, *right*). Additionally, the effective torque is also affected by the angle α between the two fields which is given by the orientation of the capacitor relative to the spectrometer field. This angle has to be known very precisely for a reliable discussion of the experimental data [3].



$0 < \varphi_{gl} < \alpha$ $\qquad$ $\alpha - 90^\circ < \varphi_{gl} < 0$

Fig. 1. Orientation of the director in dependence on the sign of the anisotropies $\Delta\varepsilon$ and $\Delta\chi$. T_E, T_B denote the torques according equ. (5,6). The equilibrium orientation depends on the ratio of the torques.

The effect on the resulting orientation is extensively described in [3, 5, 7]. An important advantage of the electric field approach is the possibility to vary the voltage in magnitude. Experiments with switching magnetic fields in NMR have been presented [12] but they are limited to relatively low field strengths and need modified NMR techniques. Starting from defined orientations, given by the orientation in the spectrometer field or in an effective static field, it is possible to follow orientational changes. It has been shown that the director dynamics in liquid crystals and liquid crystalline polymers can be described over many decades of switching times by the following equation

$$\varphi(t) = \arctan\left\{\tan(\varphi_0 - \varphi_{es})\cdot\exp\left(-\frac{t}{\tau}\right)\right\} + \varphi_{es} \qquad (7)$$

where φ_{es} is an equilibrium angle (identical to the static case or for infinite orientation times), τ is the constant describing the reorientation process. The orientation time constant τ depends on the experimental conditions (E, B_0) and material parameters such as $\Delta\varepsilon$, $\Delta\chi$, γ_1. The rotational viscosity γ_1 is one of the interesting parameters which can be obtained by this kind of experiments.

In the following, the E-field-technique is applied to materials which are both electrically and magnetically sensitive. This will be exemplified for liquid crystals and liquid crystalline polymers which show often simultaneously anisotropic behaviour in electric and magnetic fields as well.

Experimental

The NMR-experiments have been mainly carried out using a 100 MHz spectrometer (BRUKER MSL100). However, in principle, different field strengths extent the valuability of the method. Until now, fields with 60, 100, 300, 400 MHz proton frequency have been used for the *in-situ* experiments. A probe with extremely short ring delay and with improved background conditions operating at 100 MHz ^{1}H frequency (BRUKER - HP FF 100WB 1H sol5) was used (also for ^{19}F NMR) for the majority of the experiments. The resonance frequency of 100 MHz is a compromise regarding the NMR-sensitivity and the concurring effect of the magnetic field strength on the molecular orientation. The rising influence of the chemical shift at higher magnetic fields would complicate the interpretation of the spectra. Additionally, magnetically caused orientations could hamper the observation of electrically induced effects at higher fields. However, experiments in higher magnetic fields are possible and have been successfully carried out. Laboratory-made equipment for realizing a special high voltage design has been used for the experiments. We achieved an approximately rectangular shaped 1kV output in the range of 100 μs to 50 ms with rise times of 20 μs. The rise time of the pulse is almost independent of the pulse magnitude. For longer duration of voltage application (as used for the switching of polymeric liquid crystals) concatenated pulses have been applied. Maximum field strengths of about 100 MV/m can be realized. For highly insulating samples, such as electrets, D.C. voltages can also be applied up to the order of the breakdown voltage. A cylindrical coil has been used allowing experiments at different angles. Different shapes of the receiver coil are possible. However, the sensitivity of the 5 mm coil provides a valuable NMR signal up to the order of 10 ... 20 μm of electrically connected samples.

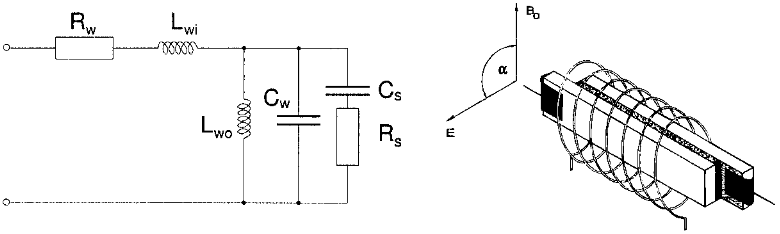


Fig. 2. The equivalent circuit of the system of the contacted sample and the electrical connections to the voltage supply (*left*). The connections and the sample itself provide some additional electronic features as explained in the text. The *right* part gives an example of a capacitor sample in an NMR coil.

The mechanical stability of the electrical contacts can be a very severe problem. Except some special situations (e.g. for the „magic angle“ narrowing“), the NMR signal is no useful indication for the voltage on the sample. Several attempts have been made to prove the connection of the electric wiring with the sample during the *in-situ* NMR-experiments, including the measurement of the resistance and the capacity. Due to the high resistance of the sample material (in the order of some MΩ) it is difficult to measure the difference from the uncontacted case. Similarly, the capacitance of the sample does not give proof of a stable connection with the sample. We used a method with a short electric excitation pulse of the electric system including the capacitor shaped sample. The observation of the free oscillation behaviour can be used to interpret the properties of the electric branch of the *in-situ* experiment. The resonance properties of the equivalent circuit have been simulated with PSPICE and are in good accordance with the experimental values. The method can also be used during the running NMR experiments where the stability requirements of the electric connection in some cases extend over some days.

The interplay between the wiring and the sample itself (C_S, R_S) can be discussed using the equivalent resonant circuit (Figure 2). The resistances R_W ; the inductances L_{wi} (contribution of the wire itself), L_{wo} (inductances resulting from the parallel wiring) and the capacitance of the wire connection C_W describe the properties of the contacted sample. The capacitance is mainly determined by the length and the distance of the wires and has to be minimized. The sample can be replaced by a parallel capacitor C_S and a parallel resistor R_S. The additional capacitance changes the resonance frequency of the circuit. The quality factor Q is strongly influenced by R_S. This results in a drastic change of the resonance properties of the circuit depending on whether the sample is well contacted or without contact. Even a slightly scratched ITO-surface can prevent the electric contact in spite of good mechanical connection. Typical values are: L_{wo} =1... 10μH, $L_{wi} \ll L_{wo}$, (L_{wi} can be neglected), C_w =1...5 pF, C_s =10...100pF. Using a storage oscilloscope the resonance behaviour with and without sample can be investigated after an electric pulse with short rise time (in the order of ns) parallel to the NMR experiment. The smaller frequency and the larger damping in the case of the contacted sample serves as clear indication of the contact between wires and the conducting ITO-surfaces.

The wire connection to the sample acts as antenna. The NMR pulses can also be detected on the oscilloscope which is used for the sample circuit. The interaction between the electrical connection and the NMR-probe resonant circuit results in a reduced signal-to-noise ratio. Some possible sources of artifacts have been investigated. There is no influence of the voltage with respect to the spectral quality as proved on phantom samples. The skin-effect induced by the NMR rf-pulses can be neglected. Similarly, the effect of dielectric heating on the material can excluded. Additional damping by the thin conducting electrode (some nm in thickness) is very indistinct and is negligible compared to the problems which arise from the contacted sample circuit.

Extra oscillations in the FID provide distortions in the spectra in the form of spikes. These oscillations occur accidentally in phase and are averaged out. Accumulation can clearly improve the quality of the spectrum. However, a reduced signal-to-noise-ratio cannot be avoided completely and is a very severe problem for insensitive nuclei (^{13}C, ^{2}H). We have extensively exploited the reversibility of reorientational processes to achieve a sufficient signal-to-noise ratio. The data acquisition should be fast compared to the reorientational processes. Some special modifications to adjust the molecular orientation during data acquisition have been introduced.

A variety of NMR experiments can be done by the synchronous timing of the electric excitation and the NMR-pulses and the data acquisition as shown schematically in Fig. 3.

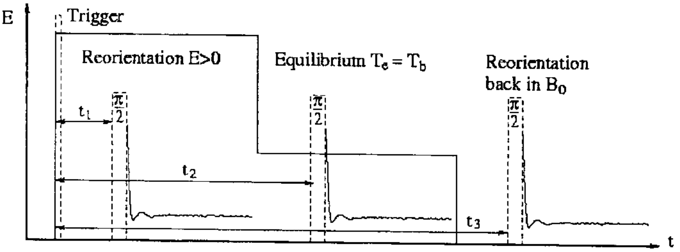


Fig. 3. The NMR-pulses and the timing of the (pulsed) electric field are synchronized. The figure gives an example of an electric field pulse started by a trigger pulse. $t_{1...3}$ denotes the delay to the NMR pulses or the start of the data acquisition. In most cases, the NMR pulse sequence is much shorter than the electric field pulse. Different delays can be introduced in order to observe different effects. The delay t_2 gives the possibility to find an equilibrium of the orientation after a shorter orientation pulse allowing data acquisition without further reorientation during data acquisition. The delay t_3 enables the investigation of magnetically induced reorientations. The starting angle can be easily adjusted by the voltage. The experiment can be modified in many ways.

The use of different delays allows the observation of electrically and magnetically induced reorientation processes as well. For the observation of magnetic reorientations the electric field can be used to orient sensitive molecules (e.g. nematic liquid crystals, dipoles of electrets) in a direction which is different from the spontaneous self-orientation in $\boldsymbol{B_0}$.

The substances investigated for this study are: the liquid crystals PCH5 and BCH5-FFF in their nematic phases, the ferroelectric mixture ZLI3654, the liquid crystalline polymers LCP105, the partially deutered Polymers synthesized by *E. Barmatov*, Moscow). A detailed description can be found in preceding papers [2, 5, 8, 13].

Results and Discussion

The molecular orientation in a LC system dominated by strong dipolar interactions (PCH5 at T = 35°C) under the influence of an electric field according equ. 2 is demonstrated in Fig. 4. The fast decay of the FID (free induction decay) is obtained at 10 Volt (below the *Freedericksz* transition) indicating that the sample is still aligned towards B_0. The slowly decaying FID reflects a turn of the director of the nematic substance to the "magic angle" of 54.7°. This provides a drastically reduced dipole-dipole interaction and gives a slowly decaying FID (increasing of T_2). The narrowing is identical for a static orientation when both torques are in an equilibrium and for a snapshot of the orientational process.

The drastic reduction of the dipolar linewidth by means of an accurate adjustment of the magic angle can be used in order to measure the anisotropic self-diffusion in the nematic phase of liquid crystals [14].

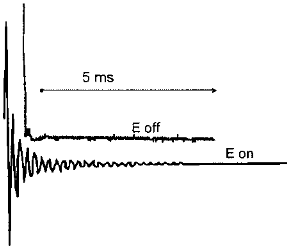


Fig. 4. ^{1}H NMR FID's of a 50 µm liquid crystal cell (PCH5, nematic between 30°C and 55°C) demonstrating the maximum narrowing effect during the reorientational process at 64 V.
The magnetic and dielectric anisotropies are positive ($\Delta\varepsilon$= 12.7 at 1kHz , $\Delta\chi(10^{-6})$=0.5 at 20°C). The upper FID is acquired without voltage.

The acquisition of relatively slow reorientational processes would be complicated by long delays between the NMR scans which are caused by the much longer reorientation in the magnetic field (some min.). A series of FID's is acquired in one scan (multi-FID) to observe the complete reorientational process. Single FID's can be decomposed after accumulation. The experimental time is reduced by the number of the FID's in such a concatenated FID. The method was valuable in order to access rotational viscosities γ_1 (50 Pas at 390 K) of the liquid crystalline polyacrylate LCP105 in its nematic phase up to temperatures close to the nematic-isotropic phase transition [2]. Reorientational time constants below 100 ms could be achieved with field strengths up to 4 MV/m. Typical spectra from the orientation process are given in Figure 5.

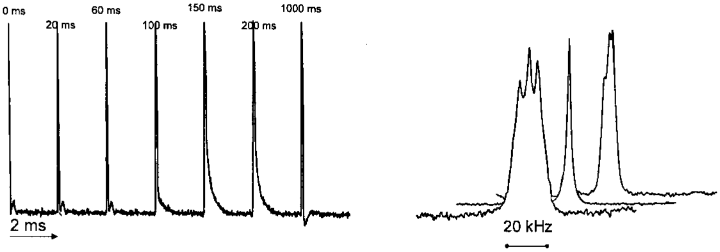


Fig. 5. left: Acquisition of a complete orientational scan in one data set. The experimental time can be drastically reduced. The method is exemplified using the electric field orientation of the liquid crystalline polymer LCP 105 at 370 K (1 FID with 2 ms acquisition time, the duration of the electric field orientation is indicated on each spectrum). The voltage was 400 Volt. The duration of the E-field has been varied by concatenation of shorter electric pulses
right: Selected spectra of the side chain polymer LCP105 taken during a fast switching process. The left spectrum has the widest splitting because of its parallel oriention to B_0 at $t_E = 0$ ms (t_E is the effective duration of the electric field. The spectrum of the magic angle passage (in the middle) has been found at $t_E = 100$ ms and the right one shows the end of the orientation ($t_E = 2$ s). The splitting depends on the angle of the capacitor surface relative to B_0 ($\forall = 75°$).

An important difference to the spectra of low molecular liquid crystals is the broadening of the linewidth by a distribution of director orientations. Intermolecular interactions are not completely averaged out by fast molecular motion. Main chain, spacer and mesogenic part of the side chain polymer contribute to a different extent to the order parameter which has been shown by site sensitive NMR experiments [15]. The resolution of the ^{1}H NMR, as used in the example, is too poor in order to discriminate between the different parts of the molecules. The reduced molecular mobility provides an additional broadening which is superposed with the distribution of the director field. The deuteration of either the main chain or the mesogenic part (or any other site) enables the direct separate access to the degree of order and the orientational behaviour of the main chain and the side chain. A partially deuterated polyacrylate [8] could be used which has been polymerized with a complete deuterated main chain (Fig. 6). As expected the reorientational viscosities, which can be measured by ^{1}H NMR, depend strongly on the degree of polymerization n (n=26 ...287). Surprisingly, there was no indication of any orientation in the main chain despite of the high sensitivity of the deuterium resonance to molecular anisotropy. It can be concluded, that the ^{1}H NMR line broadening in the magic angle passage of LCP105 is probably a superposition of a director distribution (side chain) and of the broad and unstructured spectrum of the main chain protons.

^{19}F NMR

A very sensitve approach to the question of site specific information about orientational states and processes is the use of ^{19}F NMR. The high sensitivity of the ^{19}F nucleus and the large chemical shift range provides information which cannot be obtained by means of ^{1}H NMR. However, complications can arise by the strong heteronuclear dipolar interaction which can be removed by suitable suppression techniques. For this study, no decoupling has been applied. Nevertheless, chemical shift are clearly resloved. The superimposed heteronuclear dipolar interaction is a further source of information about. However, proton decoupling provides much sharper resonances which should give a source for further detailed information [5].

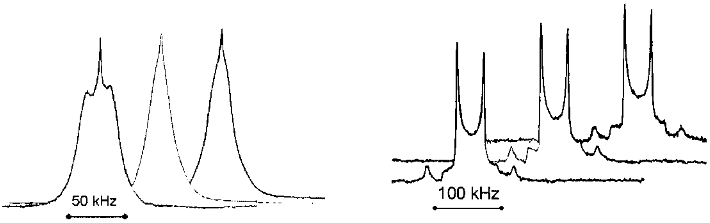


Fig. 6. Proton (left) and deuterium (right) NMR spectra (7T MHz spectrometer) at a relative orientation of the director of the sample of 0°, 45° and 90° relative to the magnetic field (n=26) in their nematic phase (temperature 20°C). The orientation has been achieved by cooling from the nematic phase at 90°C (in a field of 7.0 T) below the glass transition at 20°C. The proton spectra give the signal of the side chain part and the deuterium signal is due to the main chain. The side chain is responsible for the complete orientation whereas for the main chain site no orientation could be detected. The material were available in fractionated form at polymerization degrees of n=26, 55,154, 287. The order parameter has been found to be independent of the molecular weight within the experimental accuracy (S=0.60 ..0.67).

For that purpose a second channel is needed to remove the fluorine-proton interaction which would enable a complete mapping of highly resolved spectra in the liquid crystalline state by means of *in-situ* ^{19}F NMR NMR experiments. Only an 1-channel technique was available for the electric field experiments. It could be demonstrated that even in that case ^{19}F NMR provides interesting results [5]. Furthermore, the anisotropy of the heteronuclear interaction is a new source of information. A typical switching experiment of the low molecular liquid crystal BCH5-FFF is given in Fig.7. The orientation of the director can be extracted from the ^{1}H and the ^{19}F NMR spectra as well. The fluorine spectra carry much more site resolved information. If present, local differences in the reorientation behaviour on molecular level could be revealed .

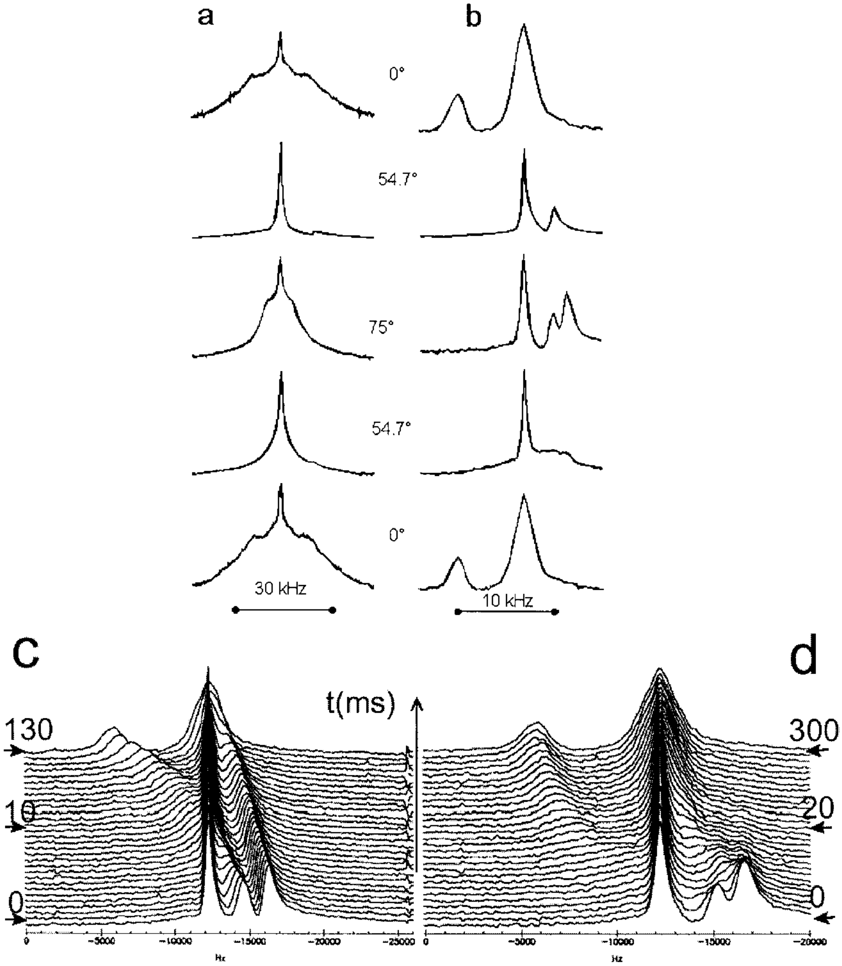


Fig. 7. ^{1}H and ^{19}F Spectra of BCH-5 FFF in its nematic phase. The line shape changes significantly during the electrically induced reorientation process: The line width of ^{1}H spectra (a) scales according to Equ. 2 whereas the position of well resolved ^{19}F lines (b) changes according to Equ. 4. The upper three rows of spectra of (a) and (b) have been taken during a reorientation in the E-field for n parallel *B* (top), 54,7° and 75°. The 75°-spectrum in the middle of (a) and (b) was taken at the beginning of the magnetic reorientation (*E*=0, last two spectra).
In some cases [5] a director distribution builts up during the reorientation process which is accompanied by a considerable line broadening as can be seen by comparing the second (no distribution) and fourth row of spectra in (a) and (b). Two complete reorientation processes in the magnetic field can be seen in (c) and
(d). The process (c) starting in an initial angle of 64° does not show any line broadening due to director distributions but reorientation (d) starting in 75° does.

Ferroelectric Liquid Crystals

The increasing interest on ferroelectric polymers is caused by the combination of the properties of polymers such as mechanical stability and ferroelectric liquid crystals showing extremely fast reaction on electrical fields. Switching times in the order of some μs can be achieved in comparison to the ms range of the switching behaviour of nematic liquid crystalline materials. The investigation of the switching behaviour is important for the technical applications using electro-optical properties. Spectroscopic methods are of interest due to their ability to give site specific information about the switching process. Recently, FT-infrared spectroscopy has been successfully applied in order to investigate the orientational behaviour *in-situ* under electric field application [16, 17]. Time resolution far below 1 ms could be achieved.

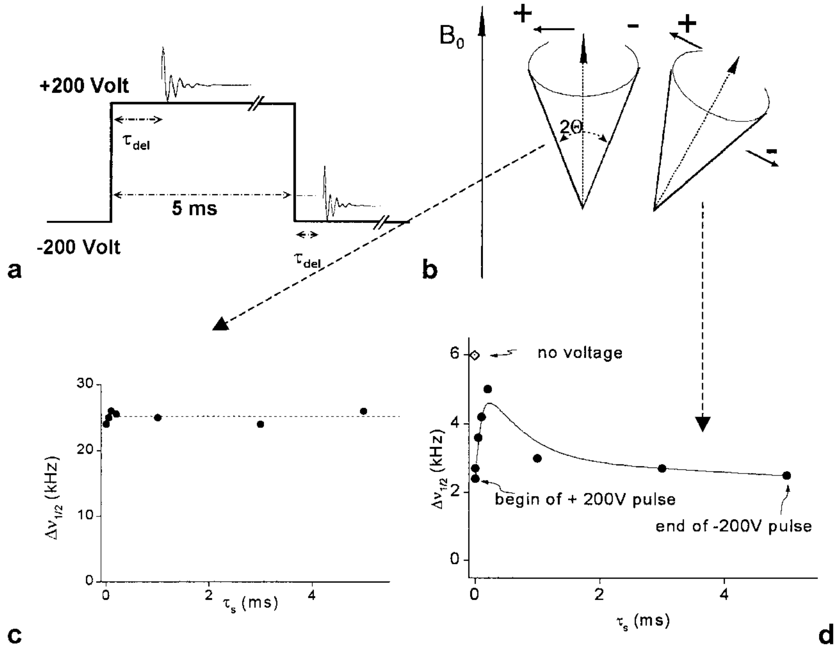


Fig. 8. Principles of the observation of a polarization switching process by means of solid-state NMR. The timing of the bipolar switching with respect to the data acquisition and the arrangement of the sample relatively to B_0 is given 8**a**. The arrows 8**b** indicate the preferred orientation achieved by the bookshelf preparation and the polarization vectors.
Two results are given . There is no change of the observed NMR parameter (^{1}H NMR linewidth) if the orientation is parallel to B_0 (8**c**). A drastic change in the linewidth occurs during the switching process for a tilted angle to B_0 (e.g. if the bookshelf arrangement is adjusted closely to the magic angle of 54.7° , **d**).

It should be mentioned that the capacitor cell for the NMR experiments has also been used for electro-optical investigations (switching times and threshold voltages) and in a polarizing microscope. The switching process in a ferroelectric liquid crystalline mixture (ZLI 3654 [13]) is schematically sketched in Fig. 8. The smectic- C^* -phase ranges from –30°C to 62°C. The ferroelectric switching process can be considered as a motion of a polarization vector around a cone. A so-called bookshelf orientation, which is a prerequisite for a well defined switching process, has been achieved by means of orientation in the spectrometer field in a defined preparation (cooling rate [13]) procedure. An important difference to the experiments on nematic substances consists in the application of voltages with a different sign to switch the polarisation state similarly as it can be done for electrets [4]. The knowledge about the tilt angle is important for the design of the experiment. In both situations in Fig. 8b, the start and final state are identical to each other which is caused by the orientation of the capacitor in the cylindrical NMR coil.

However, the spectra are different when the polarisation vector is moving around a cone during the switching process. Two examples for possible geometries are given in Figure 8b. The dashed lines refer to the results. If the bookshelf has a parallel orientation with respect to the direction of the magnetic field (2.4 T), all angles provide the same projection of the relevant vectors resulting in an unchanged ^{1}H NMR linewidth (*Fig.* 8c) within the experimental error. In Fig. 8*d*, an angle has been chosen which would yield a maximum narrowing if the motion of the resulting dipole passes a magic angle situation. A drastic change in the linewidth occurs as predicted. A certain knowledge about the tilt angle and the temperature dependent switching time is necessary in order to design a successfull experiment. The data for setting up the position of the capacitor angle relatively to B_0 in order to maximize the narrowing of the linewidth during the switching, and the temperature to slow down the orientation process has been taken from the catalogue (E. Merck). The switching time at room temperature is given as 44 μs. The experiment has been made at a temperature of 0°C in order to slow down the process to the order of about 150 μs. However, there is no principle limitation to observe faster processes. The tilt angle at 25°C is 25°. The tilt angle is temperature dependent ($\theta = \theta_0 (T_C - T)^\delta$), $\delta \approx 0.25$ for $T \leq T_C$) which is also accessible by a static electric field NMR-technique [13] (27° at 0°C for ZLI 3654). The spontaneous polarization increase also with decreasing the temperature (29 nCcm^{-2} at 20°C and 38 nCcm^{-2} at 0°C). As a sideline of the experiment, the material parameter given in the data sheet and in [13] could be confirmed.

Conclusion

The investigation of molecular orientations and/or morphological changes under the incfluence of electric fields can be either reversible or irreversible, similarly to the practical use of fields in displays or for producing polarised polymeric materials (e.g. PVDF). The investigation of controlled reorientation processes is accompagnied by technical complications in the NMR, which are mainly caused by a detoriation of the signal-to-noise-ratio. On the other hand, the experimental design is extremely flexible and can be applied to a variety of substances and problems and can be adapted for some classes of materials such as ferroelectric polymers, nematic and ferroelectric liquid crystals and LCP's. The reversibility of the effects has been used extensively. The *in-situ* experiments on liquid crystals and their polymers can be considered also as model techniques for the investigation of reversible processes by means of NMR, e.g. reversible chemical reactions. It should be emphasized that the experiments are carried out on capacitors as real electrical components. The value of the method can be drastically enhanced when further methods (e.g. IR, microscopy) can be involved.

Acknowledgements

The Deutsche Forschungsgemeinschaft is acknowledged for financial support, E. Merck Ltd., Darmstadt (Germany) and E. Barmatov (Moscow) for providing substances .

References

[1] P. Holstein, J. Rauchfuß, M. Winkler, G. Klotzsche, D. Geschke, *Solid-State NMR* **1998**, 10, 225.

[2] P. Holstein , M. Bender, M. Winkler and D. Geschke *Poly. Adv. Technol.*, **1998**, 9, 659.

[3] M. Bender, P. Holstein, D. Geschke, *J. Chem. Phys.* **2000**, 113, 2430.

[4] P. Holstein, N. Leister, D. Geschke, H. Binder, G. A. Monti, R. K. Harris *ISE10 Proc.*, **1999**, IEEE Service Center, Piscataway, New Jersey, USA

[5] M. Bender, P. Holstein, D. Geschke, *Molec. Cryst. Liq. Cryst.* **2001**, 363, 85

[6] P. Holstein, A. C. D. Lopes, J. Rauchfuß, D. Geschke, *Magn.Res.Chem.* **1997**, 35, 420.

[7] M. Bender, P. Holstein, D. Geschke, *Liquid Crystals* **2001**, 28, 1813

[8] P. Holstein, E. B. Barmatov, D. Geschke , M. Bender, V. P. Shibaev, *Colloid and Polymer Science* **2000**, 278, 711.

[9] R.Y.Dong, *NMR of Liquid Crystals*,Springer Verlag New York, Inc. (1994)

[10] A. F. Martins, P. Esnault and F. Volino, *Phys.Rev.Lett.***1986**,57, 1745

[11] N. Schwenk, C. Boeffel, H.W. Spiess, *Liquid Crystals*, **1992**,12,735

[12] H. Gotzig, S. Grunenberg-Hassanein, F. Noack, . *Z.Naturforsch.*, **1994**, 49a,1179

[13] M. Winkler, A. Gil, D. Geschke, *Liquid Crystals*, **1996**, 21 203

[14] P. Holstein, M. Bender, P. Galvosas, D. Geschke, J. Kärger, *J. Magn Reson.* **2000**, 143, 427.

[15] J. J. Titman, S. Feaux de Lacroix, H.-W. Spiess, *J.Chem.Phys.* ,**1993**, 98, 3816

[16] S. Shilov, H. Skupin, F. Kremer, E. Gebhards, R. Zentel, *Liquid Crystals* **1997**,22, 203

[17] M. Mitsuishi, S. Ito, M. Yamamoto, T. Fischer, W. Knoll *Mol. Cryst. Liq. Cryst.*, **1997**, 308,1