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Invited Lecture

Two-dimensional NMR study of slow phenyl-flips in liquid-crystalline side group polymers

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Glass-forming liquid-crystalline group polymers were investigated by ^2H 2D exchange NMR. In oriented systems, the exchange pattern of a single 2D spectrum yields the orientational distribution function with at least as high precision as a full rotation pattern of 1D spectra. In addition, important information about the geometry of the phenyl-flip motion is obtained. The 2D lineshapes are particularly sensitive towards possible slow motion of the flip axis which could be envisaged to fluctuate within the orientational distribution of the mesogenic group. However, the experimental spectra for a frozen nematic and a frozen smectic polysiloxane with an orientational distribution of width $\pm 18.5^\circ$ and $\pm 12.5^\circ$, respectively show no indication of the corresponding features, proving that the flip axis is fixed within $\pm 3^\circ$ even after a large number of flips.

1. Introduction

Liquid-crystalline polymers are of growing interest due to possible applications as high modulus fibres, optical storage media and non-linear optical materials [1–3]. Accordingly, they have been investigated extensively in recent years. Solid state NMR spectroscopy has turned out to be a particularly powerful tool for studying molecular dynamics and order in these systems [4–6]. Deuterium NMR measurements, after selectively labelling the structural element of interest, provide the most detailed information. Lineshape simulations yield correlation times, the distribution of correlation times, as well as the complete orientational distribution function in the case of macroscopically aligned systems. For the determination of the orientational distribution function, a set of angular dependent spectra is usually needed, since a single NMR spectrum does not yield unambiguous information. One- and multi-dimensional ^{13}C -MAS NMR methods [5, 7–9] yield this information in one single NMR spectrum without the necessity of isotopic labelling, but they require intensive simulation procedures. More recently an experiment based on 2D exchange NMR [10] has been introduced which allows the analysis of molecular order with high accuracy in the absence of motion [11].

In this contribution two-dimensional ^2H -HMR spectroscopy is applied to oriented liquid-crystalline side group polymers. It will be shown that it is possible to extract unambiguous information on the molecular order from a single NMR spectrum. In contrast to 1D NMR spectra, the 2D spectrum is not only sensitive to the orientational distribution but also to the geometry of the phenyl-flip motion most characteristic in side group liquid crystalline polymers [6]. The 2D spectrum yields information on the orientation of the unit under investigation with respect to the long axis of the molecule and it is sensitive to whether the axis of motion is rigid or not. The latter is particularly

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important for the understanding of the relaxation of non-equilibrium states such as poled polymers for non-linear optical applications [12].

2. Theory

Deuteron 2D-exchange NMR has proved to be a powerful tool to determine the geometry of ultra-slow molecular motions in the solid state; for a recent review see [13]. Figure 1 displays the schematic pulse sequence used to define the evolution and mixing periods in a general two-dimensional NMR experiment. The spectra obtained by this method can be interpreted as two-time distribution functions [14], tracing a molecular orientation before and after a mixing time t_m . We refer readers to references [14–17] for a detailed description of the experiment and interpretation of the 2D exchange spectra. It is noted that the exchange pattern can be used to differentiate between discrete jump and diffusive motions. For the case of phenyl flips, an elliptical exchange pattern is observed, even if the flip angle deviates from its mean value of 180° , due to ill-defined packing in an amorphous polymer [18–20].

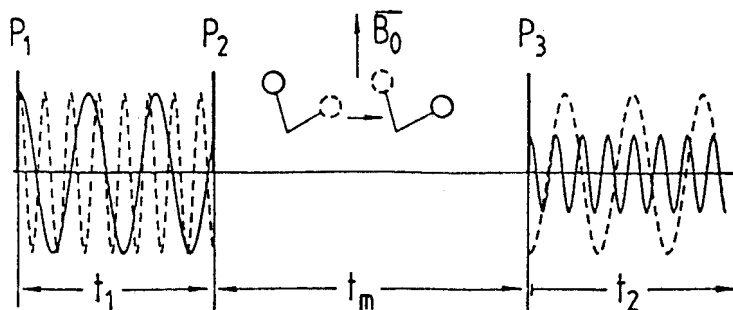


Figure 1. Schematic pulse sequence of the 2D exchange experiment: t_1 is the evolution time, t_m is the mixing time and t_2 is the detection time.

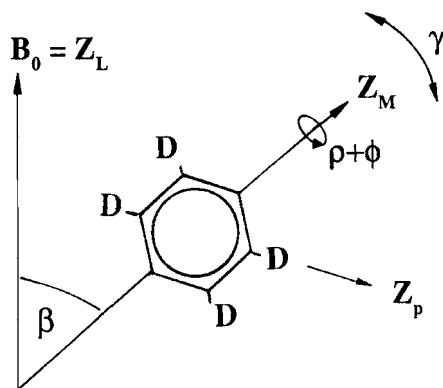


Figure 2. Molecular geometry of the deuterons attached to a phenyl ring with respect to the \mathbf{B}_0 field. The angles are denoted as used in the text. \mathbf{Z}_p is the z-axis of the principle axis system, taken into coincidence with $\text{C}-^2\text{H}$ bond. \mathbf{Z}_M is the z-axis of the molecular axis system taken into coincidence with the *para*-axis. \mathbf{Z}_L is the z-axis of the laboratory system, taken into coincidence with the \mathbf{B}_0 -field. The angles are denoted as described in the text.

In calamitic liquid-crystalline side-group polymers, magneto-aligned samples ($\Delta\chi > 0$) can be obtained such that the director \mathbf{n} is parallel to the magnetic field by slowly cooling the sample in a strong magnetic field from the isotropic melt into the glassy state. For such an oriented sample the orientational distribution $P(\beta)$ of the long axis of the mesogenic group can be read off by the orientation of the *para*-axis of the phenylene ring (see figure 2). Here we neglect a possible small deviation of the *para*-axis of the phenylene ring from the long axis of the mesogenic unit [6]. The distribution of this molecular axis may be described by a Gaussian distribution of β around the director (i.e. β is centred at 0°)

$$P(\beta) = \exp \left\{ -\frac{\sin^2 \beta}{2 \sin^2 \Delta\beta} \right\}, \quad (1)$$

where β is the angle between the molecular axis and the director, while $\Delta\beta$ describes the width of the orientational distribution. For comparison with the results of other methods, the orientational distribution [21] can be expanded in terms of Legendre polynomials and a knowledge of $\Delta\beta$ provides the determination of the expansion coefficients $\langle P_L \rangle$, the L th order orientational order parameters for all even L . Assuming an axially symmetric field gradient tensor for a deuteron ($I=1$) the frequency of a NMR transition is given by:

$$\left. \begin{aligned} \omega &= \omega_0 \pm \omega_Q, \\ \omega_Q &= \frac{\delta}{2} (3 \cos^2 \theta - 1), \end{aligned} \right\} \quad (2)$$

where $\delta = (3e^2qQ/4\hbar)$ and e^2qQ/\hbar is the quadrupolar coupling constant; ω_0 is the frequency of the central transition and θ is the angle between the $C-^2H$ bond and the magnetic field \mathbf{B}_0 . The value of ω_Q is zero when θ is the magic angle of 54.7° . Furthermore, the dependence of ω_Q on θ is particularly pronounced near $\theta = 45^\circ$. Since the *para*-axis of the phenylene ring in the oriented liquid crystal polymer is almost aligned parallel to the magnetic field, the $C-^2H$ bonds form angles close to 60° with \mathbf{B}_0 . Thus narrow 2H spectra in both dimensions are expected, which are easy to record but are highly sensitive to orientation. For a perfect orientation of the *para*-axis parallel to the magnetic field, no change in ω_Q results from internal ring rotations, since θ remains unchanged. However, for those molecules where the *para*-axis of the phenylene ring is not exactly parallel to \mathbf{B}_0 , the frequency will change as a result of phenyl-flips.

To evaluate the frequency in equation (2), it is often useful to introduce the molecular geometry and symmetry through additional molecular-fixed frames. In the simplest case, a molecular frame may be chosen such that its z_M -axis is along the *para*-axis of the phenylene ring in question, and ω_Q becomes [22]

$$\omega_Q = \delta \sum_{m=-2}^2 D_{0m}^{(2)}(\Omega_{ML}) D_{m0}^{(2)}(\Omega_{PM}), \quad (3)$$

where Ω_{ML} denotes Eulerian angles that transform between the molecular frame and the director (laboratory) frame $\mathbf{n} \parallel \mathbf{B}_0$, Ω_{PM} denotes Eulerian angles for transformation between the principal axis system of the electric field gradient tensor and the molecular frame, and $D_{mn}^{(2)}$ are the Wigner rotational matrices [23]. Rewriting equation (3) in terms of reduced rotational matrices, we obtain

$$\omega(\beta, \alpha) = \delta \sum_{m=-2}^2 d_{0m}^{(2)}(\beta) d_{m0}^{(2)}(\alpha) \cos [m(\varphi + \rho)], \quad (4)$$

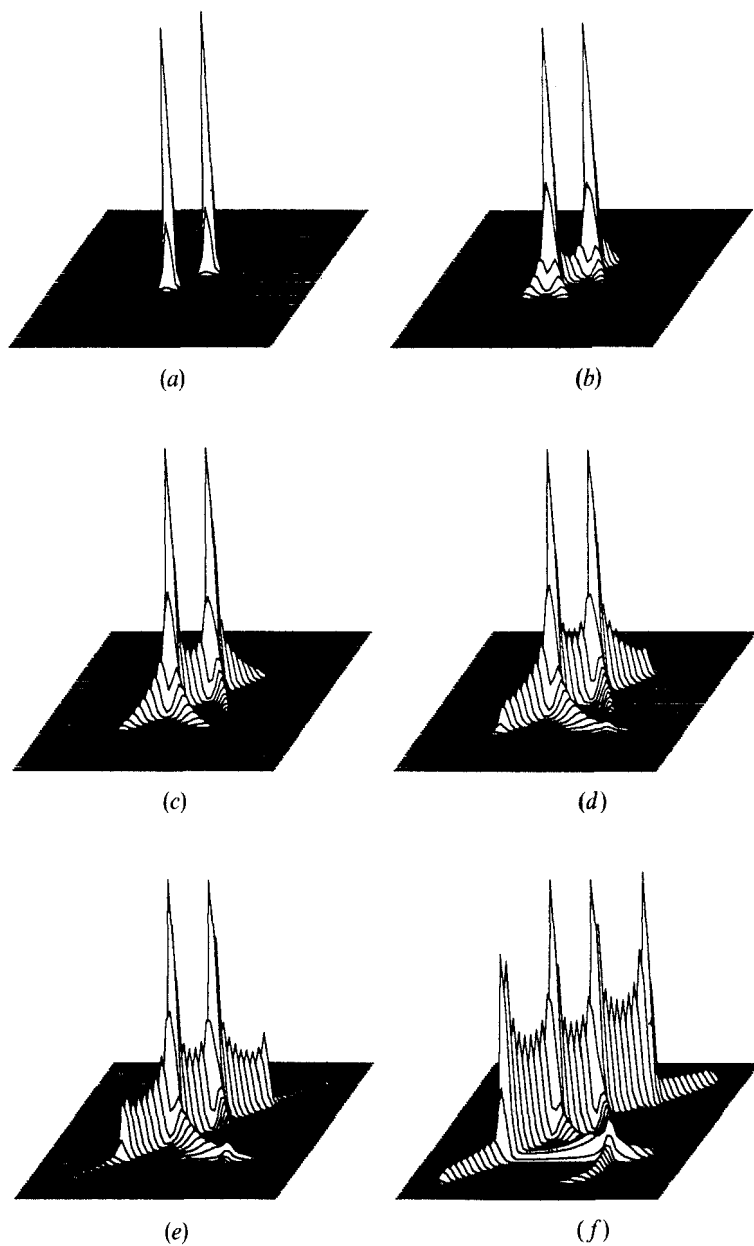


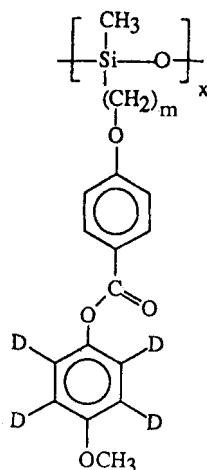
Figure 3. Simulated 2D spectra for oriented polysiloxanes with the assumption of the *para*-axis being parallel to the molecular axis. The width $\Delta\beta$ of the orientational distribution function was varied resulting in different shapes of the partial ellipses. The finite linewidth of the ^2H NMR lines is taken care of by appropriate line broadening. Note that the orientational distribution function is reflected in the exchange patterns as well as in the lineshapes of the diagonal spectrum: (a) $\Delta\beta \rightarrow 0^\circ$, (b) $\Delta\beta = 3^\circ$, (c) $\Delta\beta = 5^\circ$, (d) $\Delta\beta = 10^\circ$, (e) $\Delta\beta = 20^\circ$, (f) $\Delta\beta = 30^\circ$.

where $\alpha = 60^\circ$ is the angle between the *para*-axis and the phenyl deuteron and β is given by a distribution around 0° according to equation (1). ρ describes the rotation around the *para*-axis. By stepping through ρ from 0° to 360° a set of frequencies is obtained, which represents a static one-dimensional NMR spectrum or the main diagonal in a 2D-spectrum for the case of jump-type motion.

In a deuterium 2D-exchange NMR experiment, the C-²H bond orientation is traced before and after a mixing time t_m . For a phenyl-flip during t_m , the azimuthal angle changes from $\varphi = 0^\circ$ to $\varphi = 180^\circ$ resulting in a new frequency ω_d , which in general is different from the original frequency ω_e . In order to simulate the 2D spectrum we calculate both ω_e ($\varphi = 0^\circ$) and ω_d ($\varphi = 180^\circ$) resulting from the phenyl flip. The (ω_e, ω_d) and (ω_d, ω_e) pairs are stored in a 128×128 matrix with the appropriate spectral intensities calculated according to the orientational distribution $P(\beta)$. Simulated full 2D exchange spectra are shown in figure 3. Both diagonal and off-diagonal intensities change significantly with the parameter $\Delta\beta$, the width of the orientational distribution for the molecular z_M -axis while using the same motional parameters. The larger $\Delta\beta$ the broader the diagonal lineshape, and the partial ellipses grow to the outer vertices, until the exchange pattern comes close to that of an isotropic powder for a very large $\Delta\beta$. A full elliptical pattern is apparent for $\Delta\beta \geq 30^\circ$ (cf. figure 3 (f)). Both the diagonal and off-diagonal intensities of a 2D spectrum contain the information about the orientational distribution, since for a jump-type process the diagonal is identical to a spectrum obtained by a conventional one-dimensional NMR experiment.

3. Experimental

Two liquid-crystalline side group polymers (see Scheme 1), poly-(4-methoxyphenyl-*d*₄ 4-hexamethyleneoxybenzoate) siloxane (PS6) and poly-(4-methoxyphenyl-*d*₄ 4-trimethyleneoxybenzoate) siloxane (PS3) were investigated. Both polymers, PS3 and PS6, have been studied previously by 1D NMR [6], which offers the possibility of



Scheme. Molecular structure of the polysiloxanes investigated. m is 3 and 6 for PS3 and PS6, respectively. The degree of polymerization P_n was about 70 resulting in a molecular weight of $M_n \approx 24000$ for PS3 and $M_n \approx 27000$ for PS6.

comparing results obtained by 2D techniques with those reported earlier. DSC of PS3 yields a glass transition at 292 K and a transition from the nematic to the isotropic state at 365 K. The liquid-crystalline phase is identified as a nematic phase by polarizing optical microscopy and X-ray studies. PS6 exhibits a glass transition at 276 K and a clearing temperature at 385 K. At 328 K an additional weak transition can be observed in the DSC trace. The high temperature phase was identified as nematic and the low temperature phase as a smectic C phase. Hence the glassy state of PS6 is a frozen smectic C phase, while the glassy state of the PS3 is a frozen nematic phase.

The two-dimensional ^2H NMR experiment was performed using a Bruker CXP-300 spectrometer and procedures described elsewhere [17]. The sample was macroscopically aligned by the 7 T magnetic field of the NMR spectrometer. The 2D-spectra were analysed to yield the orientational distribution function on a VAX computer.

4. Results and discussion

Dynamic processes in the mesophase of calamitic liquid crystals are dominated by the fast anisotropic motion of the molecules around their long axis. This process is frozen in at the glass transition in liquid-crystalline side group polymers, whereas local motions still persist as revealed by NMR and dielectric spectroscopy [6, 24–26]. Due to the amorphous character of these systems, the time scale of such local processes must be described by a distribution of correlation times. Since data on the motional and orientational behaviour of the compounds under investigation are already available, they are particularly suited for testing the sensitivity of 2D experiments on oriented systems and comparison of information that can be obtained by 1D and 2D ^2H NMR methods.

4.1. Orientational distribution from 2D exchange spectra

In figure 4 the experimental 2D-spectra for PS3 and PS6, taken under the same experimental conditions (250 K, $t_m = 100$ ms), are displayed. Not only are the lineshapes along the diagonal different, but also the partial elliptical pattern is more pronounced for PS3 than for PS6. This becomes evident if one looks at the intersection of the two partial ellipses on the anti-diagonal. Comparison with the simulated spectra in figure 3 allows a simple determination of the width of the orientational distribution, which yields $\Delta\beta = 12.5^\circ$ for PS6 and $\Delta\beta = 18.5^\circ$ for PS3. This corresponds to order parameters [6] $\langle P_2 \rangle = 0.8$ and 0.65 for PS6 and PS3, respectively. As expected, these $\langle P_2 \rangle$ values reflect the degrees of orientational order for frozen smectic C and nematic phases. The same parameters could be obtained from simulation of a set of one-dimensional spectra, taken with the sample rotated to different angles of the orientation axis with respect to the magnetic field [6]. The experiment presented here has the advantage that no goniometer is needed for the measurement of the 2D spectrum, which is obtained for the oriented state after cooling the sample from the isotropic phase.

The determination of orientational distributions out of the 2D spectra is general and not limited to liquid-crystalline side group polymers. It is applicable to oriented samples whenever slow motions are present. An extension to nuclei other than deuterons is possible. It should be noted, that if no motion is present, this motion can be introduced artificially by rotating the sample mechanically during the mixing time t_m , as recently demonstrated in [11].

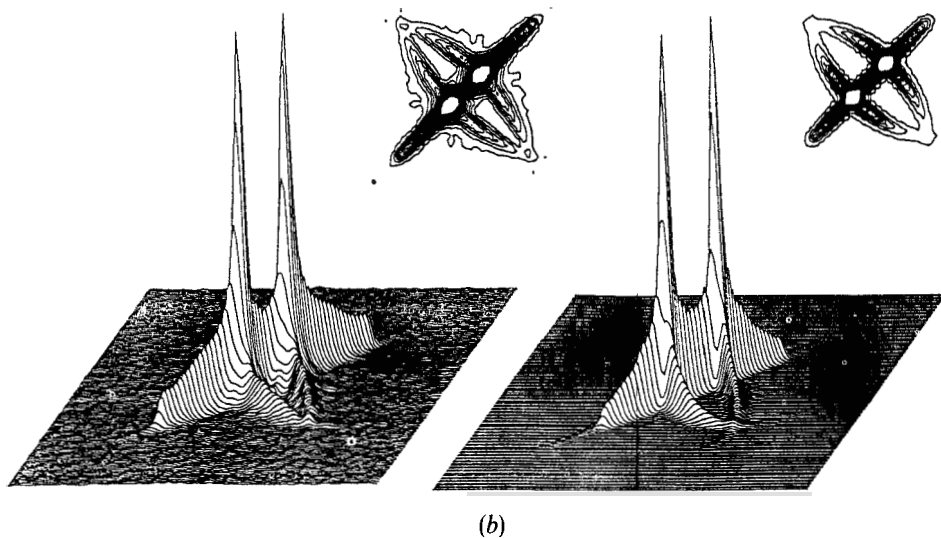
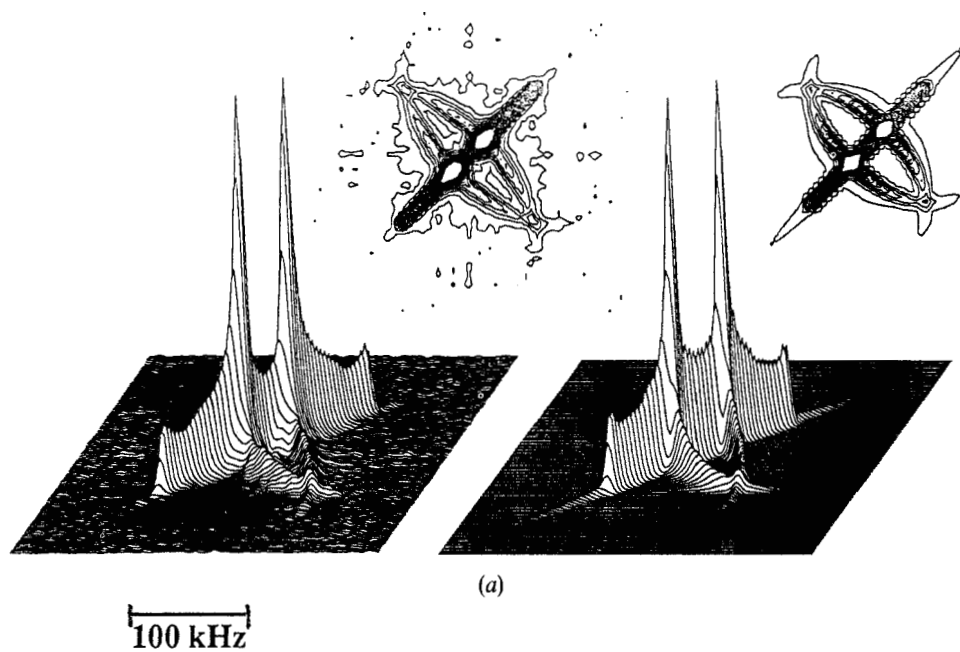


Figure 4. Experimental and simulated spectra for PS3 (a) and PS6 (b) taken at $T = 250$ K with $t_m = 100$ ms and a waiting time of 0.5 s after each individual scan. The overall measuring time for one spectrum was 12 h. The simulations were performed by assuming a width parameter $\Delta\beta = 12.5^\circ$ for PS6 and $\Delta\beta = 18.5^\circ$ for PS3, which is in good agreement with data obtained from one-dimensional NMR spectra. Contour plots are shown as insets.

4.2. Phenyl flips: possible distributions of rotational angles

2D exchange NMR is particularly informative concerning the geometry of slow motions. Concerning the phenyl flips in non-crystalline materials, two questions arise (see fig. 2):

- (i) Is the flip angle well-defined, i.e. $\phi = 180^\circ$ or is it distributed around $\phi = 180^\circ$ as a mean value?
- (ii) Does the flip occur around a fixed *para*-phenylene axis or does this axis fluctuate about an angle $\pm\gamma$?

In fact, in amorphous polycarbonate (PC) Hansen *et al.* [18–20] have shown that the flip angle exhibits a substantial distribution, $\phi = 180^\circ \pm 25^\circ$, reflecting the ill-defined packing in this polymer. Moreover, the width of the rotational angle distribution was associated with the strength of the mechanical relaxation of PC. Therefore, we will consider question (i) first. As noted above (see figure 3), the phenyl flip leads to elliptical exchange ridges. Only part of these however, can be detected for highly oriented liquid-crystalline polymers with $\mathbf{n} \parallel \mathbf{B}_0$. A distribution of flip angles leads to a smearing out of the ellipses, in particular in the region of their short axes, remote from the central regions [18–20]. Since these parts are missing in the spectra of the oriented samples, 2D exchange spectra have also been recorded for an isotropic sample of PS3—see figure 5(a). Although weak, the elliptical pattern is clearly detected throughout its circumference. This indicates that the distribution of the flip angles in the liquid crystalline polymer is considerably narrower than in amorphous polycarbonate, where only part of the elliptical ridge could be detected [18–20].

When estimating the flip angle distribution from the 2D spectra, one has to remember that the flip angle ϕ is not directly detected in the NMR spectrum, but the reorientational angle θ between C–²H bond directions before and after the flip. Elementary trigonometry shows that ϕ and θ are related by:

$$\begin{aligned} \cos \theta &= \sin^2 60^\circ \cos \phi + \cos^2 60^\circ \\ &= \frac{3}{4} \cos \phi + \frac{1}{4}. \end{aligned} \quad (5)$$

A given distribution in ϕ around 180° transforms into a considerably narrower distribution around $\theta = 120^\circ$, whereas distributions around $\phi = \theta = 0^\circ$ have approximately equal widths. For the 2D exchange spectrum of figure 5(a), the mixing time t_m was chosen such that the phenylene rings have typically flipped many times, $t_m \approx 50 \tau_c$, where τ_c is the mean correlation time. Thus, the flip angle distributions around $\phi = 0^\circ$ and $\phi = 180^\circ$ should be equal in width.

The simulated 2D spectrum with a Gaussian flip angle distribution (width at half height of $\Delta\phi = \pm 10^\circ$), fitted to the experimental spectrum, is plotted in figure 5(b). Note that due to the fact that the distribution around $\phi = 180^\circ$ transforms in a narrowed distribution in θ , only widths $\Delta\phi \geq \pm 10^\circ$ lead to detectable changes in the elliptical exchange pattern. Therefore one cannot exclude that $\Delta\phi$ is even narrower than $\pm 10^\circ$, although the best fit for the 2D-spectra can be achieved for this value. It is remarkable that in the frozen nematic liquid-crystalline polymer the flip angle distribution is much narrower than in glassy polymers like PC. In fact, it is almost as narrow as the reorientational angle distributions for chain motions in crystalline polymers [27]. This shows that the packing in partially ordered frozen liquid-crystalline polymers is much better defined than in amorphous systems. The much better defined geometry of the motion in the frozen liquid crystalline polymers, as compared with amorphous PC, has

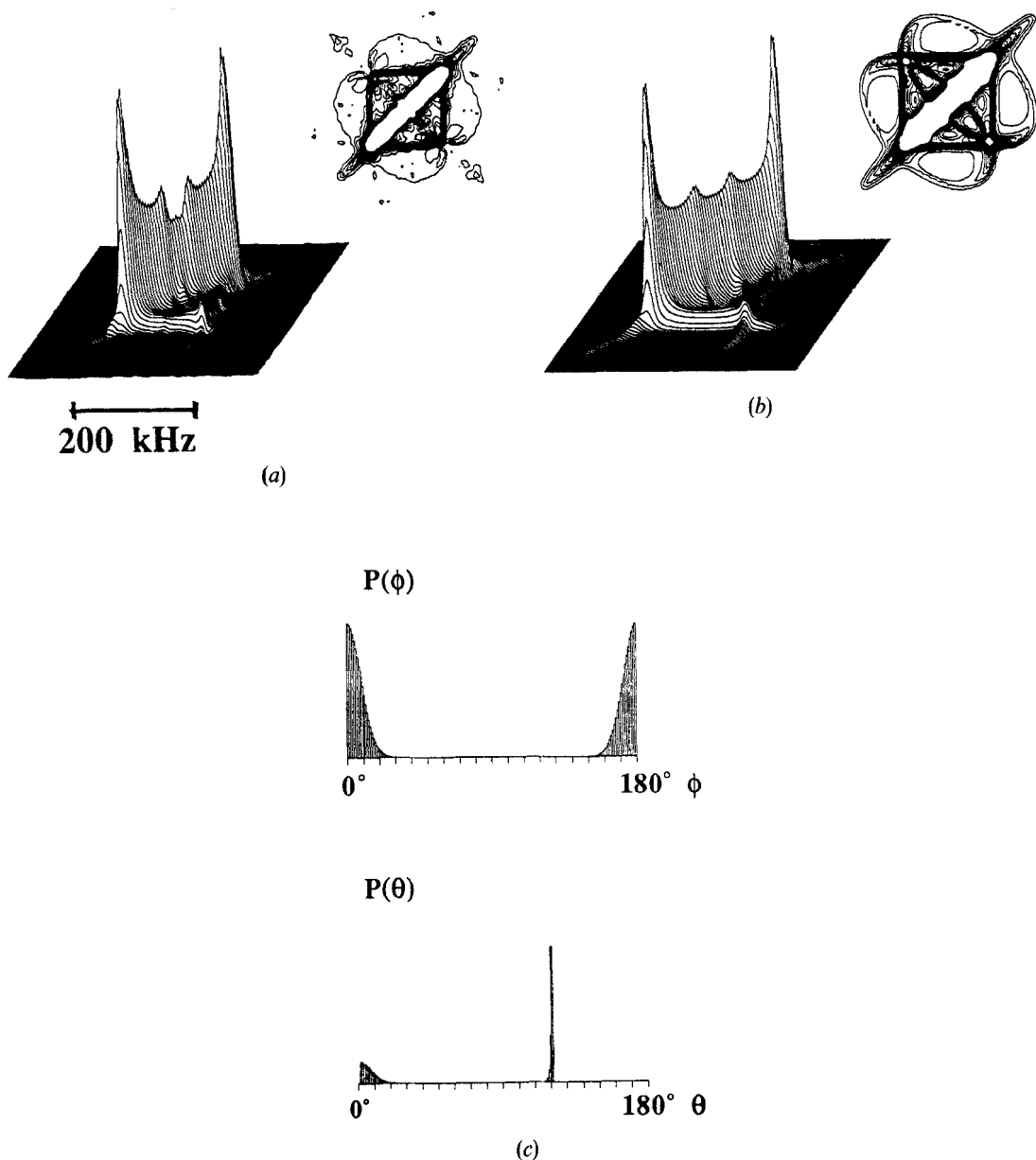


Figure 5. (a) Experimental spectrum of the unoriented sample for PS6 taken at $T = 250$ K with $t_m = 100$ ms. The measuring time was 80 h. The contour plot is shown as the inset. (b) Simulated spectrum taking into account a distribution of rotation angles $\Delta\phi = \pm 10^\circ$. (c) Distribution $P(\phi)$ and the corresponding distribution $P(\theta)$, which is used for the simulation shown in (b).

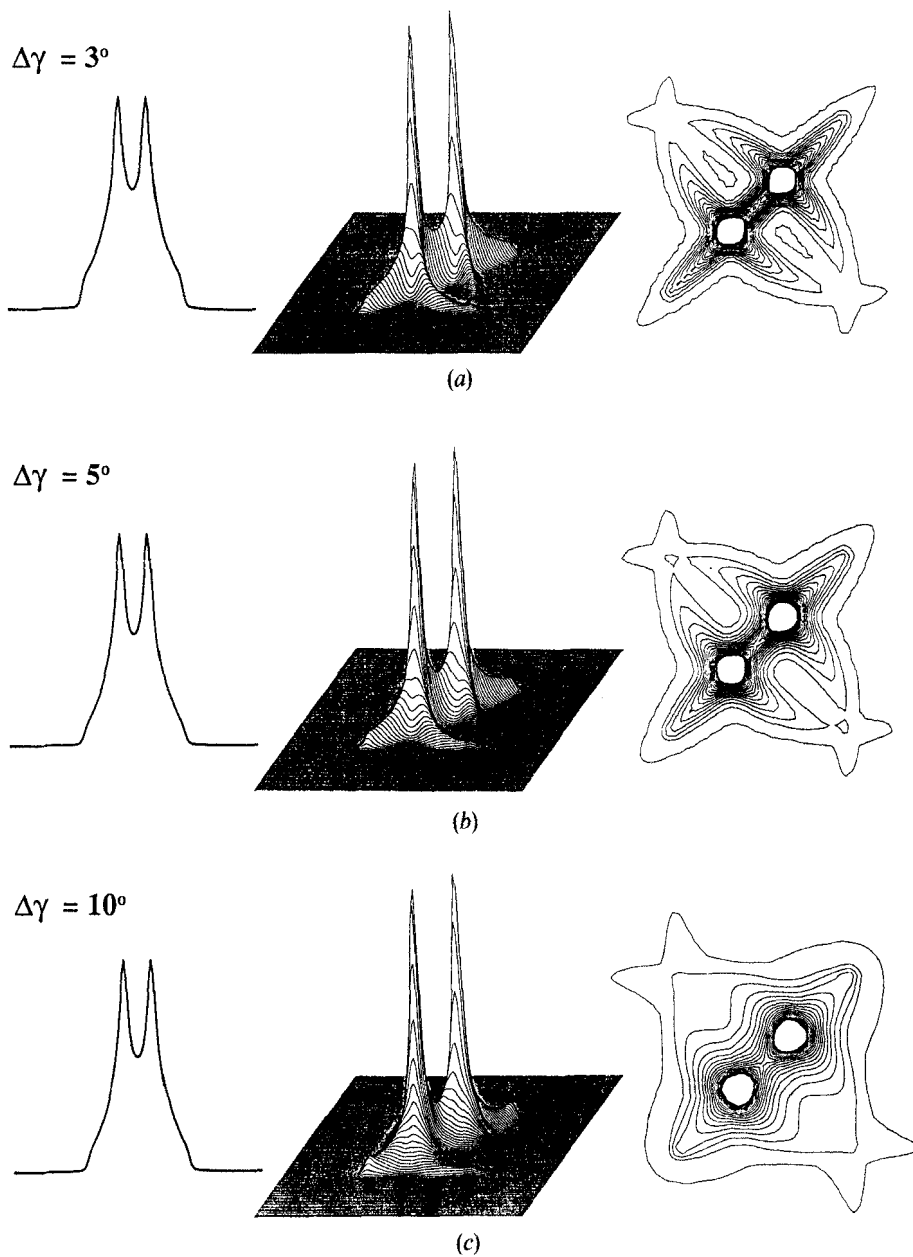


Figure 6. Simulated spectra taking into account the motion of the *para*-axis. It is assumed that a diffusive type of motion within the orientational distribution can be described by spherical Gaussians around $\gamma=0^\circ$. The simulations are performed for a width of the orientational distribution $\Delta\beta=12^\circ$ and different extents of diffusive motions: (a) $\Delta\gamma=3^\circ$, (b) $\Delta\gamma=5^\circ$ and (c) $\Delta\gamma=10^\circ$. The left column presents the 1D lineshapes obtained by the projection of the 2D spectra on the ω_1 -axis. This lineshape is identical to the one observed for a one dimensional spectrum taken under the conditions of the 2D spectrum. The centre column presents stacked plots of the 2D spectra and the right column the corresponding contour plots.

to be especially appreciated in view of the fact that the timescale of the flip motion is alike in both systems and the activation energies are very similar [6, 18–20].

4.3. Phenylflips: possible motion of *para*-axis

Let us now consider question (ii) raised above, concerning a possible motion of the *para*-axis. This question is particularly important with respect to the long term stability of the molecular alignment in frozen liquid-crystalline polymers. One could imagine that the *para*-axis fluctuates within the limits imposed by the orientational distribution. Since for $\mathbf{n} \parallel \mathbf{B}_0$ the spectrum is narrowest, the exchange ridges (part of ellipses) are insensitive to distributions in the flip angle, yet they sensitively probe changes of the *para*-axis. This is demonstrated in figure 6, where simulated 2D spectra are plotted for different Gaussian distributions of the *para*-axis with variances $\Delta\gamma$, see figure 2. For comparison 1D lineshapes for the same angular uncertainties are plotted as well. Whereas they are completely insensitive towards changes of the orientation of the *para*-axis of the phenylene ring occurring on a slower time scale, the ridges in the 2D patterns broaden considerably with increasing $\Delta\gamma$, cf. the spectrum for $\Delta\gamma = 10^\circ$. Since the experimental spectra, see figure 4, do not show any sign of such a broadening, we conclude that the *para*-axis remains fixed within $\pm 3^\circ$ even after many flips, emphasizing again the rather well-defined packing in liquid-crystalline polymers.

5. Conclusion

2D exchange NMR of liquid-crystalline polymers yields highly specific information about the geometry of local motions. The comparison of 2D powder spectra with those of oriented samples leads to complementary results. From the 2D powder spectra deviations in the flip angles from the jumps of the phenyl rings can be extracted. 2D spectra for macroscopically oriented samples with $\mathbf{n} \parallel \mathbf{B}_0$ yield the orientational distribution function and can detect possible fluctuations of the *para*-axis of the phenylene ring, about which the flip motion occurs. Remarkably in both the nematic and the smectic liquid-crystalline polymer the distribution in the flip angle $\Delta\phi = \pm 10^\circ$ is much narrower than in amorphous PC ($\Delta\phi = \pm 25^\circ$), indicating considerably better defined packing in the former. Moreover, fluctuations of the *para*-axis above the angular resolution of the experiment ($\pm 3^\circ$) could be excluded even on a timescale $t_m \approx 50 \tau_c$, where the rings have undergone a large number of flips. This result is particularly noteworthy, since it is known that poled non-linear optical polymers of similar molecular architecture to the systems under investigation show orientational relaxation resulting in a loss of their electro-optical properties on a long time scale [11, 28]. It is difficult to imagine that this effect is a result of the phenyl-flip motion only, which is restricted to one degree of freedom. However, since this loss of optical properties takes place on a time-scale much longer than that of the 2D-experiment, director fluctuations which are still slow on the time scale of the 2D experiment cannot be excluded. It should be noted that the NMR studies were performed 25 to 40 K below the glass transition. It has been shown that in this temperature regime poling relaxation is already significantly slowed down [28]. Further studies closer to the glass transition may reveal a higher sensitivity towards the motion of the *para*-axis since the correlation times for these processes are expected to increase while approaching the glass transition T_g .

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