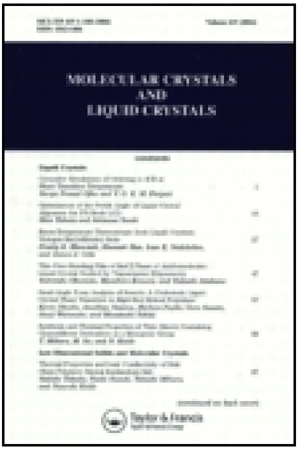

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Two-Dimensional NMR Relaxation Spectroscopy of Liquid Crystal Polymers

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TWO-DIMENSIONAL NMR RELAXATION SPECTROSCOPY OF LIQUID CRYSTAL POLYMERS

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Abstract Specifically deuterated liquid crystal polymers (LCPs) were studied by 2D NMR relaxation spectroscopy. Analysis of the various ^2H NMR experiments provided quantitative information about molecular order and dynamics of the systems. The polymers exhibit typical semicrystalline behavior, manifested by two different motional components. Molecular structure is characterized by a high degree of conformational and orientational order, which strongly correlates to the unusual mechanical properties of these materials. The NMR investigations emphasize the particular advantages of 2D NMR relaxation methods in studying complex chemical systems.

INTRODUCTION

Dynamic ^2H NMR spectroscopy represents a powerful method in the field of modern polymer science.[1,2] Improvements in both experimental techniques and spectral analysis yield detailed information about the molecular properties of the materials studied, comprising structural and dynamical aspects.[3,4] Up to now, most investigations have been concerned with classical one-dimensional (1D) techniques. However, the development of two-dimensional (2D) NMR methods offers a variety of new perspectives.[5,6] Few attempts have been made to apply 2D techniques to dynamic ^{2}H NMR spectroscopy.[7,8] In the following we present the first application of these methods to liquid crystal main chain polymers (LCPs).

These polymers have attracted increasing attention during the last years due to the observed good mechanical properties which suggest potential applications as high modulus fibres and mouldings.[9,10] As already known from previous NMR investigations, LCPs are characterized by a complex molecular behavior.[3,11] The 2D NMR studies, reported here, are aimed to improve and complete the existing molecular description of these polymers. The final objective of the investigations is to relate the characteristic molecular properties, sorted out by NMR, with the unusual bulk behavior of these polymer systems.

In the first section, the theoretical background of 2D NMR relaxation spectroscopy is briefly outlined. The following section presents typical experiments performed on LCPs. Finally, in the last section, characteristic molecular properties of these systems are discussed in relation to their mechanical behavior.

THEORETICAL BACKGROUND

Generally, conventional 1D NMR experiments can be described by the excitation or preparation of the spin system using a train of r.f. pulses, separated by various constant time intervals Δ_1,

Δ_2 ... Δ_i, according to the individual experiment. At the end of the pulse sequence, during the detection period t_2, a time signal $S(\Delta_1 \ldots \Delta_i, t_2)$ is recorded. After Fourier transformation of this signal the corresponding frequency NMR spectrum $S(\Delta_1 \ldots \Delta_i, \omega_2)$ is obtained.

The basic scheme of 2D NMR spectroscopy[5,6] involves three successive time periods: i) preparation period, ii) evolution period, and iii) detection period. Here, the pulse sequence contains a further variable time interval (evolution period) t_1. The 2D data are then collected by recording the time signal $S(\Delta_1 \ldots \Delta_i, t_1, t_2)$ for a series of increments t_1. Fourier transformation of $S(\Delta_1 \ldots \Delta_i, t_1, t_2)$ in both time domains yields the 2D spectrum $S(\Delta_1, \ldots \Delta_i, \omega_1, \omega_2)$.

In this work, we adapt three different pulse sequences, commonly employed in relaxation studies of $I = 1$ spin systems, to this general scheme (2D relaxation spectroscopy):

i) saturation recovery sequence

$(90)_x - t_1 - (90)_x - \Delta_1 - (90)_y - \Delta_1 - t_2$

ii) quadrupole echo sequence[12,13]

$(90)_x - t_1 - (90)_y - t_1 - t_2$ and

iii) Jeener-Broekaert sequence[14]

$(90)_x - \Delta_1 - (54)_y - t_1 - (54)_y - \Delta_2 - (90)_y - \Delta_2 - t_2$

Fourier transformation with respect to t_1 and t_2 for each of these sequences yields a 2D NMR spectrum, which may be regarded as a graph of the relevant natural widths vs the resonance positions of the individual dynamic spin packets that constitute the spectrum.[15-17] For example, cross sections through the quadrupole echo spectrum along ω_1 provide homogeneous lineshapes associated with the spin-spin relaxation time T_{2E}.[7,17] It is found that both the magnitude of T_{2E} and the way in which T_{2E} changes across the spectrum are very dependent upon the character of the molecular motion, responsible for spin relaxation.[3,17]. Similarly is true for the variation of the spin lattice relaxation times T_{1Z} and T_{1Q}, which may be obtained from sequence i) and iii), respectively.

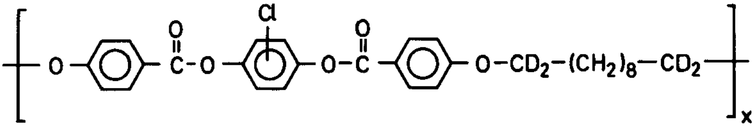
The latter pulse sequence can be used to perform a 2D exchange experiment[18] by incrementing Δ_1 at a constant mixing time $\tau_M = t_1$, as shown previously.[8] Carrying out the 2D exchange experiment at different mixing times τ_M, finally yields a 3D experiment.[6]

All three pulse sequences shown above are sensitive to molecular motions in a characteristic time range. Generally, saturation recovery sequences in a high magnetic field ($B_0 \geqq 5$ T) may be used for fast-rotational studies (10^{-12} s $< \tau_R <$ 10^{-8} s), while quadrupole echo sequences are applicable in the slower dynamic range (10^{-8} s $< \tau_R < 10^{-4}$ s).[13] Finally, by employing Jeener-Broekaert sequences, ultraslow motions (10^{-4} s $< \tau_R < 10$ s) can be detected.[19]

Analysis of these NMR experiments is achieved by employing a density matrix treatment based on the stochastic Liouville equation.[3,13] Various adjustable parameters, characterizing molecular order and dynamics, enter the problem.[3] In the specific case of LCPs, three different motional modes are considered. They describe localized conformational changes (jump process) and overall rotations and fluctuations of larger chain segments (diffusive process). The corresponding correlation times τ_J, $\tau_{R\parallel}$ and $\tau_{R\perp}$ specify the time scale of these motions. Similarly, molecular order is described by contributions to three different levels. They account for conformational order of the chain segments, orientational order of the polymer chains with respect to a preferential local axis (director axis), and alignment of the director axes in a laboratory frame. The relevant quantities are denoted as segmental ($S_{Z'Z'}$), orientational (S_{ZZ}) and macroorder parameters ($S_{Z''Z''}$), respectively.

EXPERIMENTS AND METHODS

The liquid crystal polyester I was specifically deuterated in the flexible spacer unit as described elsewhere.[20] The DSC thermograms show a glass transition (T_g) at T = 303 K, and a nematic melt, extending from 433 K to 553 K.



I

The NMR samples (250mg in a 4mm tube) were pretreated by heating to the nematic melt (T = 473 K) for about 30 min outside the NMR magnet to avoid macroscopic alignment. ^{2}H NMR measurements of the solid polymer were performed on a Bruker MSL 300 spectrometer at 46 MHz (B_0 = 7 T), using quadrature detection and appropriate phase cycling schemes. 90° pulse width of the home-built probe was 2.2 μs. The resulting 2D data consisted of 64 sampling points in the t_1 domain and 2048 sampling points in the t_2 domain. The number of scans for each FID was chosen between 800 and 1000, depending on the particular experiment. 2D spectra were obtained using standard software.[21] Thus, numerical corrections such as maximum entropy methods (MEM),[22] accounting for finite receiver deadtime, are not yet included. The corresponding numerical procedures are currently being developed.

A FORTRAN program, based on the NMR model (see previous section), was employed to analyze the ^{2}H NMR experiments. Numerical solution of the stochastic Liouville equation was achieved, using the Lanczos algorithm[23]. Further details will be given in a forthcoming paper.[24]

RESULTS

Two-dimensional ^{2}H NMR spectra of the solid LCP I (below the melting point) have been recorded using saturation recovery, quadrupole echo and Jeener-Broekaert sequences. Representative results, demonstrating the advantage of 2D NMR methods, are shown in Figures 1 and 2. The quadrupole echo spectrum (Fig. 1), referring to T = 363 K, reflects the characteristic phase behavior of LCP I below the melting point. Two spectral components are observed, corresponding to a mobile (central peaks) and a motionally restricted phase (outer peaks). Especially, the contour plot presentation (Fig. 1b) clearly displays the slower decrease of the inner peak amplitudes along ω_1. The corresponding shorter spin-spin relaxation times T_{2E} reflect a surprisingly high chain mobility in this phase.

The 2D NMR spectrum from the Jeener-Broekaert sequence (Fig. 2) contains valuable information about slow motions in the ms range. As expected, there are lineshape oscillations across the ω_2 domain, which sensitively depend on the fixed pulse separation Δ_1.[4] In addition, inspection of the ω_1 domain reveals a pronounced variation of the natural widths as function of position in the spectrum, indicative of both type and time scale of the involved motions.

From computer simulations of the 2D NMR experiments, employing the NMR model outlined above, quantitative data about molecular order and dynamics are obtained.

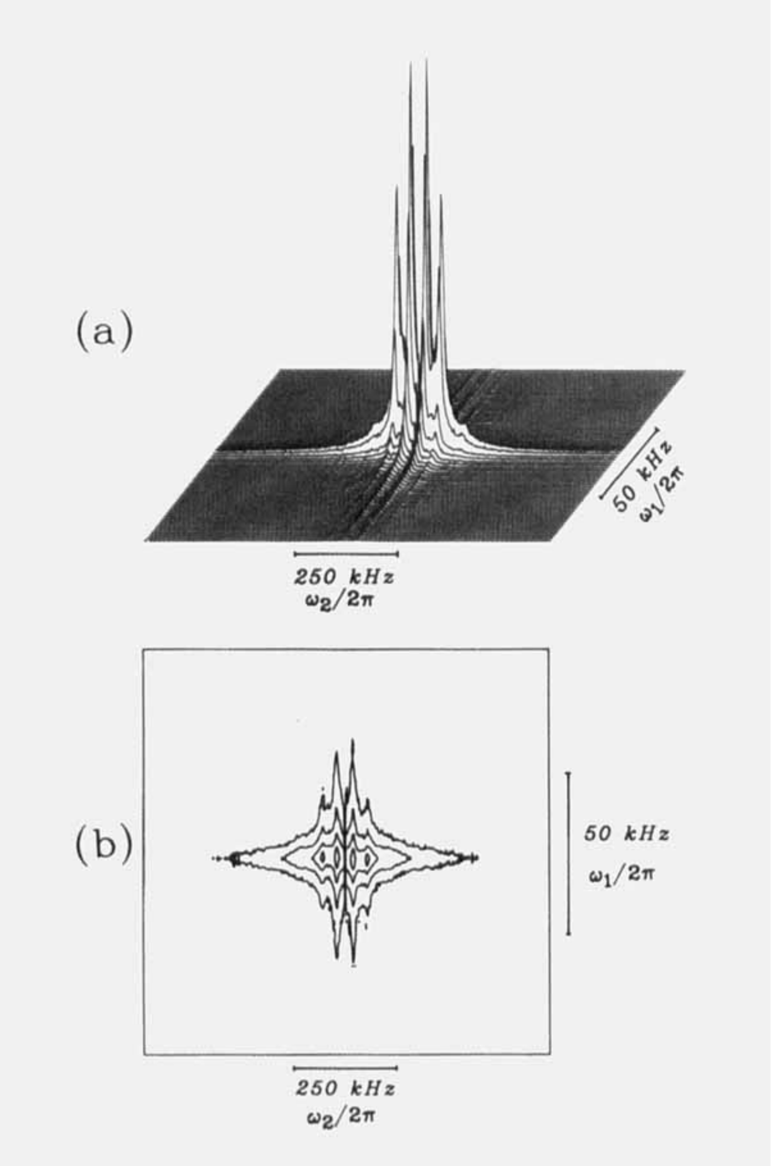


FIGURE 1. Experimental 2D NMR relaxation spectrum of LCP I at T = 363 K, obtained with the quadrupole echo sequence. a) Stack plot, b) contour plot. (Power spectrum display).

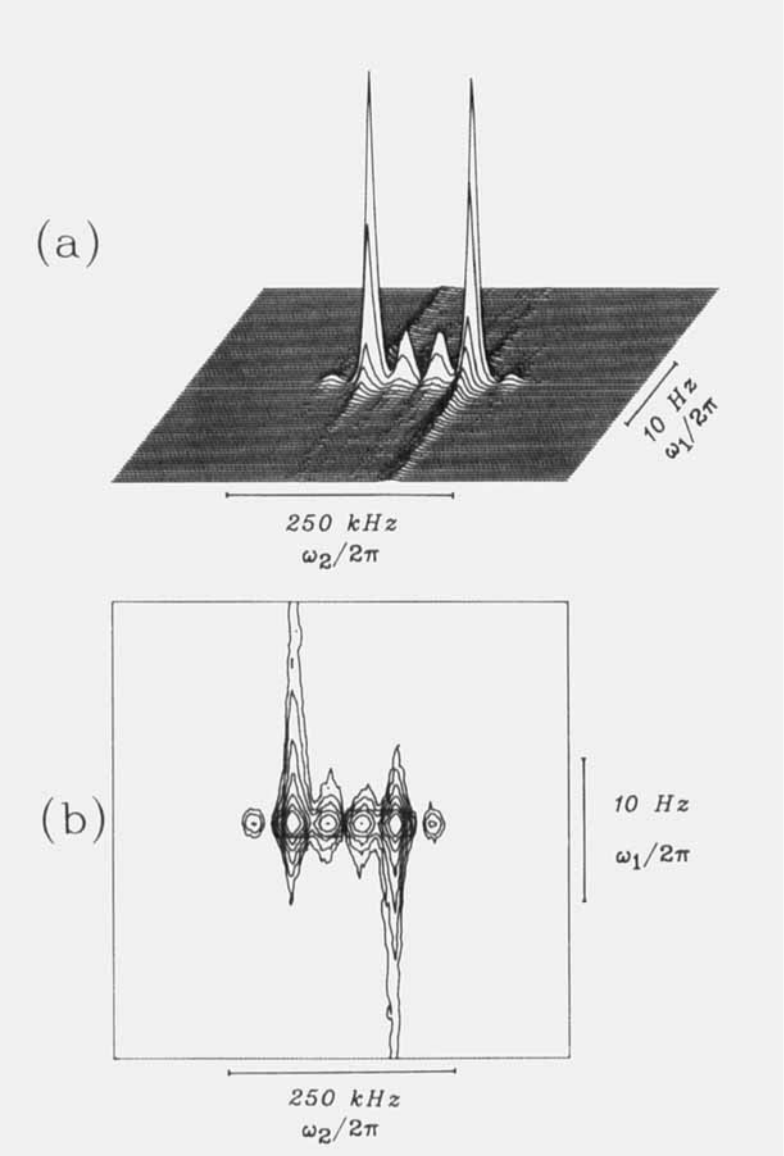


Figure 2. Experimental 2D NMR relaxation spectrum of LCP I at T = 233 K, obtained from a Jeener-Broekaert sequence (Δ_1 = 28 μs, Δ_2 = 25 μs). a) Stack plot, b) contour plot. (Power spectrum display).

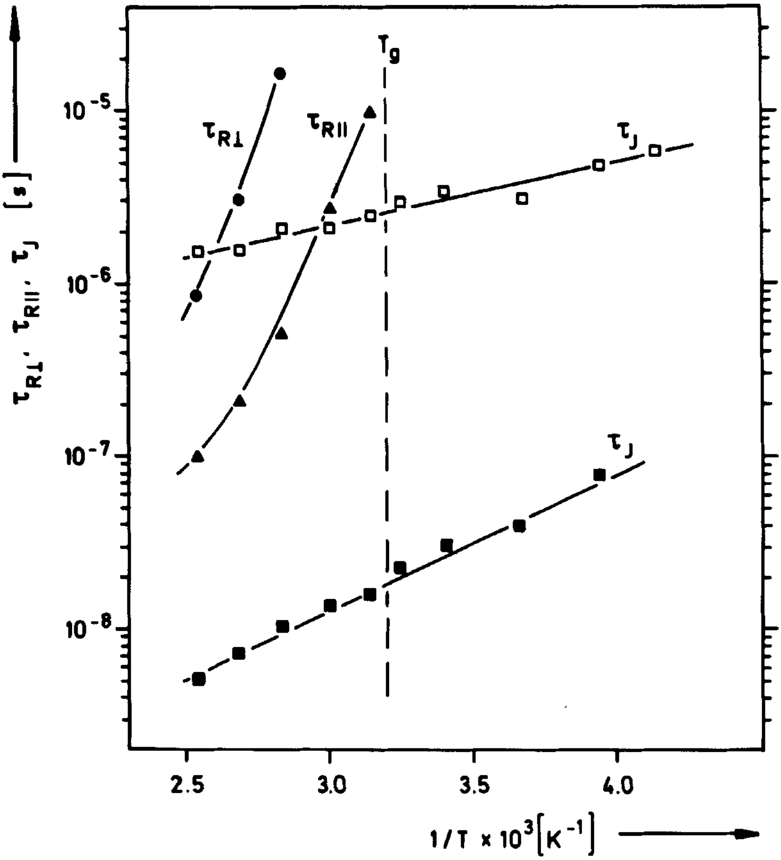


FIGURE 3. Arrhenius plot of various correlation times, characterizing the molecular dynamics of LCP I: Mobile and immobile components are denoted by full and open symbols, respectively. ▲ = Chain rotation, ● = chain fluctuation, ■ , □ = chain isomerization.

The correlation times, characterizing the various motions of solid LCP I, are summarized in Fig. 3. As mentioned above, the system appears to be heterogeneous as two motional components can be distinguished. The dynamics of the mobile component, denoted as liquid crystalline fraction, is characterized by diffusive motions of larger chain segments (chain rotation and fluctuation) and local conformational changes occurring in a surprisingly fast range of 10^{-8} s to 10^{-5} s. In contrast, the dynamics of the immobile component, classified as crystalline fraction, is dominated by slow conformational jumps in the 10^{-6} s to 10^{-5} s range. The specific activation energies, determined from the temperature dependence of the various correlation times, corroborate these results.

A particular advantage of these dynamic NMR methods is the possibility to discriminate between different types of molecular order, i.e. to separate conformational, orientational and macroorder of the chains.

The observed conformational order parameters of $S_{Z'Z'} = 0.7$ (liquid crystalline component) and $S_{Z'Z'} = 0.75$ (crystalline component) indicate highly extended chain conformations within the flexible spacer. In addition, the orientational order parameter of $S_{ZZ} = 0.9$ reflects a large measure of parallel orientation of the polymer chains. This high degree of molecular order is closely correlated with the observed mechanical properties of these LCPs, as discussed below.

DISCUSSION

The incorporation of 2D techniques into dynamic ^2H NMR experiments offers a variety of advantages.[6] Especially, the variations in natural widths (i.e. $1/T_{ij}$) over the spectrum significantly improve the reliability of the analysis.[25] This is of particular importance for the investigation of complex materials, such as the LCPs discussed here.

The heterogeneity of the solid LCPs, reflected in their dynamic behavior (Fig. 3), is confirmed by calorimetric studies, in which glass and melt transitions are observed, similar to ordinary semicrystalline polymers.[11,20] The liquid crystalline component is characterized by fast conformational jumps, occuring over the whole temperature range investigated. In addition, above T_g surprisingly fast reorientations of larger chain segments are detected, which gradually freeze at T_g, possibly due to a loss in free volume.[26] The dynamics of the crystalline component is quite different, exhibiting only restricted conformational motions in the low frequency range. This might be explained by a denser packing of this fraction, as known from ordinary crystalline polymers.[27]

The most prominent feature of the LCPs concerns their high degree of conformational and orientational order.[28] Evidently, highly extended conformers prevail in the liquid crystalline phase, as can be deduced from the conformational order parameter of $S_{z'z'} = 0.7$ for this fraction. On the other hand, a conformational order of $S_{z'z'}$

= 0.75, found for the crystalline component, is far below the limiting value of 1.0, expected for regular crystals.[29] This finding corresponds to calorimetric results, indicating non-regular crystalline regions due to conformational disorder.[11,20]

However, a high degree of orientational order (S_{ZZ} = 0.9) is found, independent of temperature and polymer phase. The observed value is considerably larger than known from low molar mass liquid crystals,[30] indicating an almost parallel orientation of the polymer chains with respect to the local director.

Finally, it should be noted that a complete macroscopic alignment of the director axes ($S_{Z''Z''}$ = 1.0) is achieved by using strong magnetic fields or melt spinning techniques.[3,11] Stress-strain measurements, performed on melt-spun fibres, revealed exceptional good mechanical properties. The observed tensile moduli (≅ 22 GPa) and strengths (≅ 0.34 GPa) are at least comparable or even better than those of conventional post-treated polymer fibres.[11] Evidently, the striking mechanical properties of the LCP fibres originate from the high degree of molecular order, sorted out by NMR investigations.

CONCLUSIONS

2D NMR relaxation spectroscopy has successfully been employed to study the molecular properties of LCPs. The results indicate a strong correlation with the exceptional mechanical properties of these compounds.

Further developments of 2D NMR methods, comprising theoretical and experimental aspects, are particularly suitable for simplifying the molecular characterization of complex chemical and biological systems.

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