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Liquid Crystals

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Solid state N.M.R. relaxation study of liquid crystal polymers employing a two dimensional technique

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Molecular motions of liquid crystal polymers in the solid state cover a broad dynamic range, extending from the fast rotational to the ultra slow motional regime. Two dimensional N.M.R. relaxation spectroscopy is designed to follow these motions and to differentiate the various motional modes. In addition, different types of molecular order, modulated by these regions, are also discriminated. The solid state dynamics of the polyesters studied depends sensitively upon their thermal history. Annealed samples show a typical semicrystalline behaviour, manifested by two different motional components. The molecular order is characterized by a high degree of conformational and orientational order of the polymer chains, which is strongly correlated with the exceptional mechanical properties of these systems.

1. Introduction

Liquid crystal polymers have been reported to exhibit a variety of unusual material properties and are subject to an increased research activity [1, 2]. One major objective of these studies is the evaluation of a correlation between their macroscopic bulk behaviour and the characteristic molecular properties of these systems. In this connection, solid state ^{2}H N.M.R. has been employed successfully to elucidate the molecular characteristics of such polymers, comprising both structural and dynamical aspects, [3–5]. By combining various pulse experiments it has been possible to follow molecular motion over an extremely wide dynamic range, not available with any other experimental technique [3, 6].

Here, we report on a promising extension of solid state dynamic N.M.R. using a two dimensional procedure [7, 8]. The method employs the pronounced anisotropy of the nuclear spin relaxation times, observed for polycrystalline or multidomain samples. In these systems, the relaxation times vary as a function of the crystal or director orientation, and equivalently as a function of the frequency across the breadth of the powder spectrum. It turns out that this variation is of particular diagnostic importance for the dynamical characterization of complex molecular systems [9, 10].

In the first section the experimental and theoretical background is presented. Then typical results are given to demonstrate the applicability of the new N.M.R. techniques. In the main section two dimensional relaxation experiments on liquid crystal main chain polymers are presented. Computer simulations provide the orientational distributions and conformations of the polymer chains and the correlation times of the various motions. They are related to the exceptional tensile properties of these systems, evaluated by mechanical measurements [5].

2. N.M.R. techniques

Multipulse dynamic N.M.R. is a time domain technique. The system is subject to a sequence of non-selective rf pulses and the response $S(t_2)$ after the last pulse is recorded. Fourier transformation of $S(t_2)$ yields the common one dimensional frequency spectrum $S(\omega_2)$. Powder lineshapes obtained via multipulse sequences may be distorted as compared with those obtained from the free induction decay due to orientation dependent relaxation times [11–13]. Generally, it is observed that with an increasing relaxation period, t_1, significant spectral changes occur, which are different for the different motions. Apparently, the change of the powder lineshape with the pulse separation, t_1, is indicative of the type of motion [3, 14, 15].

A two dimensional version of such relaxation experiments is achieved by recording the time signals as a function of successive incremented time intervals, t_1. A complex Fourier transform in both time domains transforms $S(t_1, t_2)$ into a two dimensional representation $S(\omega_1, \omega_2)$ of the corresponding relaxation experiment [7, 8]. Three different pulse sequences, commonly employed in ^{2}H N.M.R. relaxation studies, are adapted to this general scheme:

(i) inversion recovery

$$(180)\text{-}t_1\text{-}(90)_x\text{-}\Delta\text{-}(90)_y\text{-}\Delta\text{-}t_2;$$

(ii) quadrupole echo [16] and

$$(90)_x\text{-}t_1/2\text{-}(90)_y\text{-}t_1/2\text{-}t_2;$$

(iii) Jeener–Broekaert sequences [17]

$$(90)_x\text{-}\Delta_1\text{-}(54)_y\text{-}t_1\text{-}(54)_y\text{-}\Delta_2\text{-}(90)_y\text{-}\Delta_2\text{-}t_2.$$

Each sequence defines a specific dynamic window in which molecular motions can be studied. Generally, inversion recovery in a high magnetic field ($B_z \geqq 5\,T$) may be used for fast rotational studies ($10^{-12}\,\mathrm{s} < \tau_R < 10^{-8}\,\mathrm{s}$), while quadrupole echo experiments are applicable in the slower dynamic range ($10^{-8}\,\mathrm{s} < \tau_R < 10^{-4}\,\mathrm{s}$) [13]. Finally, by employing Jeener–Broekaert sequences, ultra slow motions ($10^{-4}\,\mathrm{s} < \tau_R < 10\,\mathrm{s}$) can be detected [18].

The two dimensional representation of the various relaxation experiments may be regarded as a graph of the relevant natural widths versus the resonance positions of the individual dynamic spin packets which constitute the spectrum [19]. For example, cross sections through the two dimensional quadrupole echo spectrum along ω_1 provide homogeneous lineshapes associated with the spin–spin relaxation time T_{2E} [9, 10]. 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, 10, 19].

Analysis of these N.M.R. experiments is achieved by employing a comprehensive relaxation model based on the stochastic Liouville equation [3, 13, 20]. Various adjustable parameters, characterizing molecular order and dynamics, enter the problem [3]. In the specific case of liquid crystal polymers four different motional modes, depicted in figure 1, are considered. They describe localized conformational changes (jump processes involving phenyl rings or methylene groups) and overall rotations and fluctuations of larger chain segments (diffusive process). The correlation times τ_J, $\tau_{R\parallel}$ and $\tau_{R\perp}$ specify the time scale of these motions. Collective molecular reorientations, characteristic of liquid crystals, are considered likewise. For this mechanism,

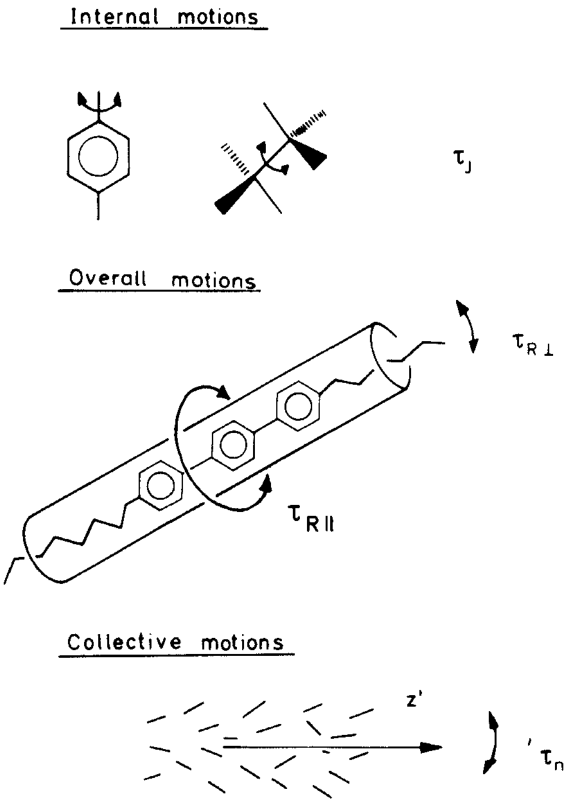


Figure 1. Schematic representation of molecular and collective motions relevant to liquid crystal polymers.

known as director order fluctuations, a continuous distribution of correlation times is predicted. However, in contrast to isolated motions of single molecules, these collective reorientations can only be observed in the anisotropic melt of liquid crystal polymers [21]. Molecular order is described by contributions to three different levels. They account for conformational order of the various chain segments, orientational order of the polymer chains with respect to a preferential local axis (that is the director), and alignment of the director axis in a laboratory frame. The relevant quantities are denoted as segmental ($S_{Z'Z'}$), orientational (S_{ZZ}) and macro-order parameters ($S_{z''z''}$), respectively [3, 5, 20].

The sensitivity of two dimensional relaxation spectra to the type and the time scale of molecular motions is illustrated in figure 2. The spectra refer to quadrupole echo sequences and characterize two possible reorientation mechanisms of a methyl group (three-site jump versus continuous diffusion). For simplicity, we have chosen equal correlation times for both motions ($\tau_J = \tau_{R\parallel} = 10^{-6}$ s). Drastic spectral differences are observed. Apparently, these two dimensional relaxation spectra are highly indicative of the type of motion. The same is true for the corresponding normalized contour plots (see the right side of figure 2) [19]. We note that similar two dimensional relaxation spectra can be obtained from inversion recovery or Jeener–Broekaert sequences. Thus, by applying this two dimensional technique to different pulse sequences, the various motions can be differentiated over an extremely wide dynamic range, extending from 10^{-12} s in the fast rotational to 10 s in the ultra slow motional

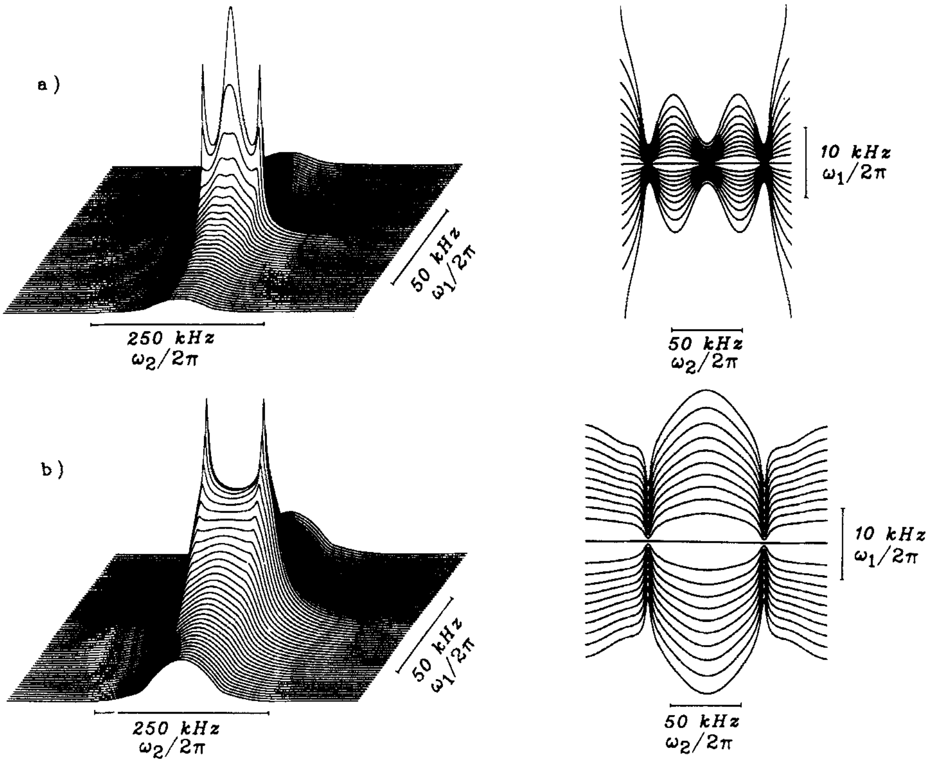
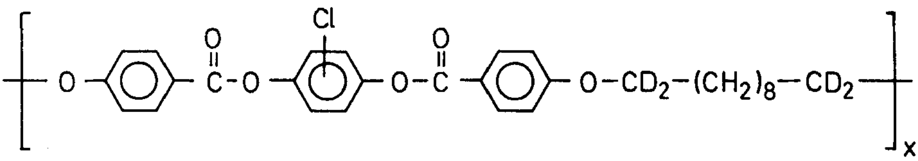


Figure 2. Calculated two dimensional relaxation spectra (quadrupole echo sequences) of a solid, containing a rotating (deuteriated) methyl group. (*a*) Three-site jump, $\tau_j = 10^{-6}$ s. (*b*) Continuous diffusion, $\tau_{R\|} = 10^{-6}$ s. Left hand side: Stack plots. Right hand side: Normalized contour plots (contours in units of 5 per cent of the maximum amplitude).

regime. Since the different motions modulate different kinds of molecular order (for example segmental order and orientational order) these orders can also be differentiated.

Experiments and methods

Liquid crystal polymers with the chemical structure



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were specifically deuteriated at the α-segment of the aliphatic spacer as described elsewhere [22]. The D.S.C. thermograms show a glass transition at T_g of 303 K and a nematic melt, ranging from T_m of 433 K to T_{NI} of 553 K. Typically, 250 mg of the polymer, sealed in a 4 mm N.M.R. tube, were heated to the nematic melt (T = 473 K) outside the N.M.R. magnet and then rapidly cooled to room temperature within a few seconds. Annealed samples were obtained by heat treatment of the quenched samples at 423 K for about 40 min.

The ^2H N.M.R. measurements were performed on a Bruker MSL 300 spectrometer at $\nu = 46\,\text{MHz}$ ($B_z = 7\,\text{T}$), using quadrature detection and appropriate phase cycling routines. The 90° pulse width of the home-built probe was 2·2 μs. The number of scans varied between 800 and 1600. The resulting two dimensional data set consisted of 64 sampling points in the t_1 domain and 2048 sampling points in the t_2 domain. Generally, zero filling for better resolution was employed in t_1. The two dimensional Fourier transform was performed by removing the imaginary data points after the first complex Fourier transform in t_2. The second Fourier transform, only applied to the real data set, yielded the pure absorption two dimensional spectrum $S(\omega_1, \omega_2)$ [23]. Normalized contour plots [19] were obtained by dividing the ω_2-spectra at the various ω_1 values by the centre ω_2-spectrum ($\omega_1 = 0$). From this contour representation the anisotropy of the corresponding relaxation rates can be read directly.

A FORTRAN program package was employed to analyse the ^2H N.M.R. measurements [3, 20]. The programs simulate two dimensional N.M.R. relaxation experiments of $I = 1$ spin systems undergoing inter- and intramolecular motion in an anisotropic medium [24]. Numerical solution of the stochastic Liouville equation was achieved using the Lanczos algorithm [25].

3. Results and discussion

Two dimensional N.M.R. relaxation methods have been employed to evaluate the complex solid state behaviour of liquid crystal polymers. The studies were intended to reveal the effect of the thermal history on the molecular properties, determined by the N.M.R. techniques. Only multidomain samples ($S_{z''z''} = 0$) were examined, taking full advantage of the highly informative character of angular dependent relaxation rates.

Figure 3 shows two dimensional N.M.R. relaxation spectra of solid liquid crystal polymers, obtained from inversion recovery sequences at 363 K. The stack and contour plots refer to a quenched (see figure 3 (*a*)) and an annealed sample (see figure 3 (*b*)), respectively. Depending on the thermal history, characteristic differences are observed. The quenched sample exhibits a complex spectral feature, associated with mobile deuterons. In contrast, the two dimensional spectra of the annealed sample indicate two different components referring to mobile and immobile deuterons in distinct regions of the polymer, which we assign to a liquid-crystalline and a crystalline phase [3, 5, 10]. In this respect, liquid crystal polymers resemble conventional polymers, which also exhibit amorphous and crystalline phases, [5, 26].

The assignment is supported by additional two dimensional relaxation experiments on annealed samples, employing the pulse sequences discussed previously. Representative examples are shown in figure 4. The two dimensional spectra refer to quadrupole echo sequences and two selected temperatures, one above (see figure 4 (*a*)) and one below the glass transition T_g (see figure 4 (*b*)). Note, that only one spectral component is observed for $T < T_g$. Apparently, the mobility of the liquid-crystalline fraction is drastically reduced on approaching T_g.

Quantitative data concerning molecular order and dynamics of the solid liquid crystal polymers were obtained by computer simulation of the various two dimensional NMR experiments. As we have mentioned the annealed samples appear to be heterogeneous as two different fractions (liquid-crystalline and crystalline) are detected. Diffusive motions of larger chain segments ($\tau_{R\parallel}$, $\tau_{R\perp}$) and local conformational changes (τ_J) contribute to the dynamics of the liquid-crystalline component. Detailed

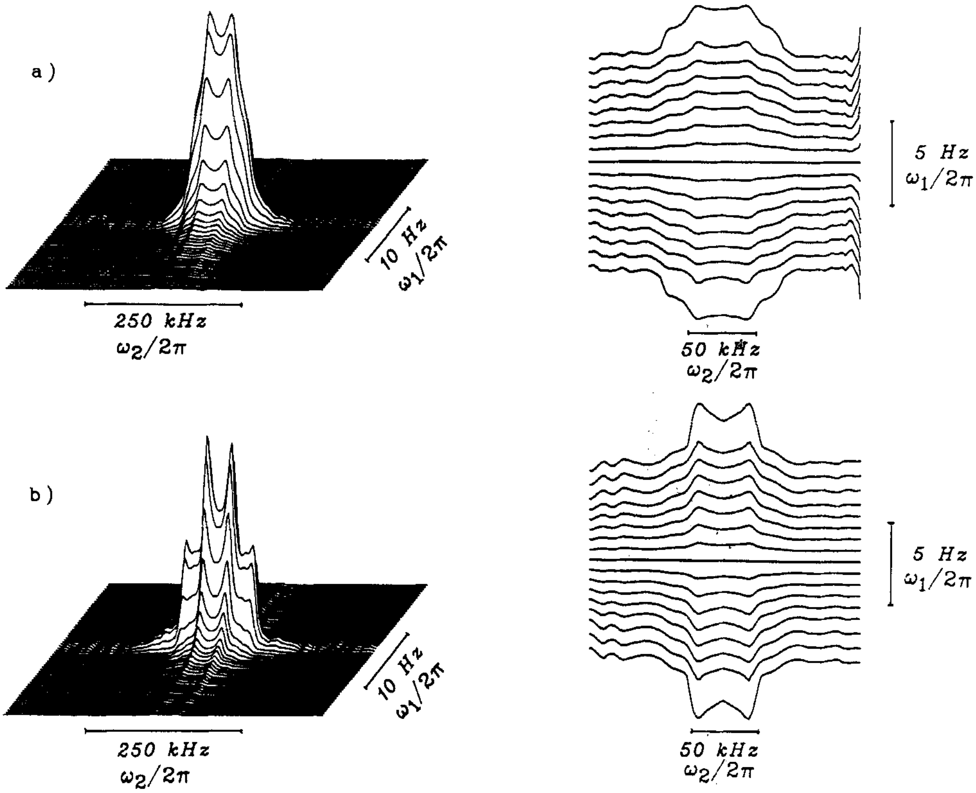

Figure 3. Experimental two dimensional relaxation spectra (inversion recovery sequences) of the liquid crystal polymer, deuteriated at the α-segment of the aliphatic spacer. (*a*) Quenched sample at $T = 363\,\mathrm{K}$. (*b*) Annealed sample at $T = 363\,\mathrm{K}$. Left hand side: Stack plots. Right hand side: Normalized contour plots (contours in units of 10 per cent of the maximum amplitude).

analysis reveals a surprisingly fast dynamic range, extending from 10^{-8} s to 10^{-4} s. However, the Arrhenius plot for the overall diffusive motions ($\tau_{\mathrm{R}\parallel}$, $\tau_{\mathrm{R}\perp}$) is not linear, the apparent activation energies increase with decreasing temperature. Thus, all intermolecular motions gradually freeze out at T_g, possibly due to a loss of free volume [27]. The dynamics of the crystalline component is quite different, exhibiting only restricted conformational motions in the low frequency range ($10^{-6}\,\mathrm{s} < \tau_J < 10^{-5}\,\mathrm{s}$). This might be explained by a denser packing of this fraction, as observed for conventional crystalline polymers [28].

Simultaneously, the structural parameters of the liquid crystal polymers could be determined. The most prominent feature concerns the high degree of conformational order [29]. Evidently, highly extended conformers prevail in the liquid-crystalline phase, as can be deduced from a segmental order parameter of $S_{Z'Z'}$ of 0·7 for this fraction. On the other hand, a conformational order parameter of $S_{Z'Z'}$ of 0·75, found for the crystalline component, is far below the limiting value of 1·0, expected for regular crystals [30]. This observation is corroborated by calorimetric studies, indicating non-regular crystalline regions due to conformational disorder [5]. However, a high degree of orientational order ($S_{ZZ} = 0{\cdot}9$) is found, independent of thermal history and polymer phase [29]. The observed value considerably exceeds that exhibited

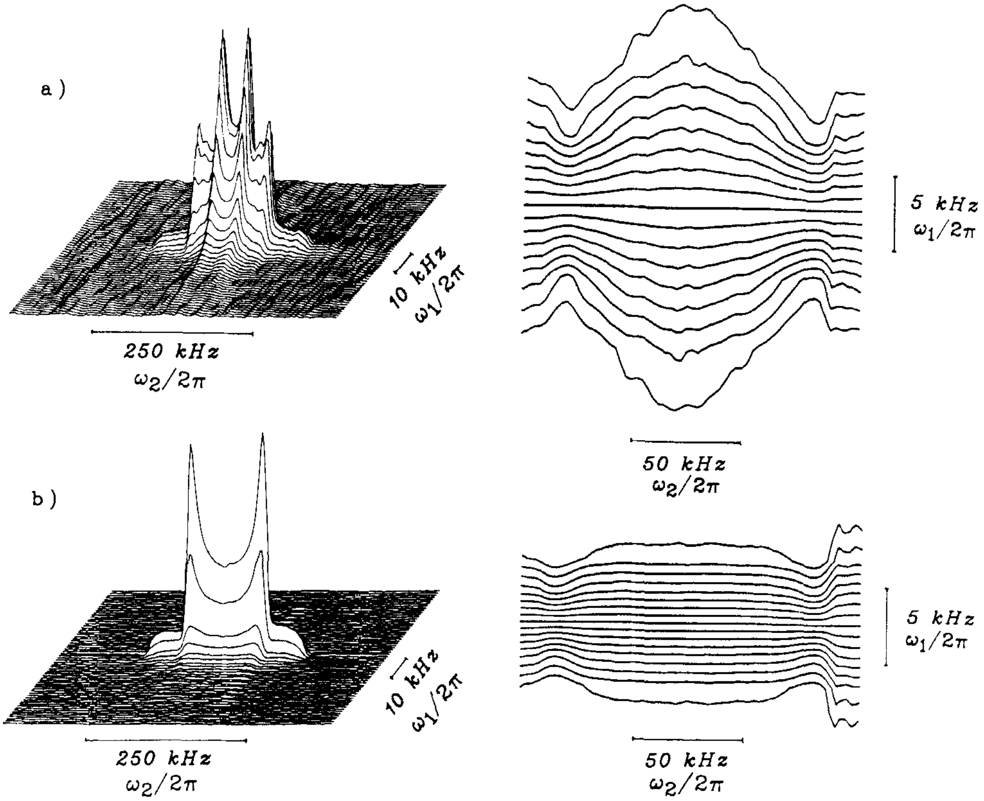

Figure 4. Experimental two dimensional relaxation spectra (quadrupole echo sequences) of the liquid crystal polymer, deuteriated at the α-segment of the aliphatic spacer. (*a*) Annealed sample at $T = 363\,\mathrm{K}$ ($T > T_g$). (*b*) Annealed sample at $T = 298\,\mathrm{K}$ ($T < T_g$). Left hand side: Stack plots. Right hand side: Normalized contour plots (contours in units of 10 per cent of the maximum amplitude).

by low molecular weight nematogens [31]. As predicted [32–34], the polymer chains are highly ordered on a molecular level in agreement with previous E.S.R. studies [35].

Finally, it should be noted that complete macroscopic alignment of the director axes ($S_{z''z''} = 1\cdot 0$) is achieved by using strong magnetic or shear fields [3, 5, 29]. Stress-strain measurements, performed on melt-spun fibres, revealed exceptionally good mechanical properties. The observed tensile moduli (up to 22 GPa) and strengths (up to 0·34 GPa) are at least comparable or even better than those of conventional post-treated polymer fibres [5]. Evidently, the striking mechanical properties of the liquid crystal polymer fibres are closely related to the high degree of molecular order, indicated by the new N.M.R. techniques.

4. Conclusions

Two dimensional N.M.R. relaxation spectroscopy has successfully been employed to study the molelcular properties of liquid crystal polymers in the solid state. The results, referring to quenched and annealed samples, indicate a strong correlation to the exceptional mechanical properties of these systems. It appears that the new

N.M.R. techniques present a powerful tool for characterizing complex chemical systems such as liquid crystal polymers.

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