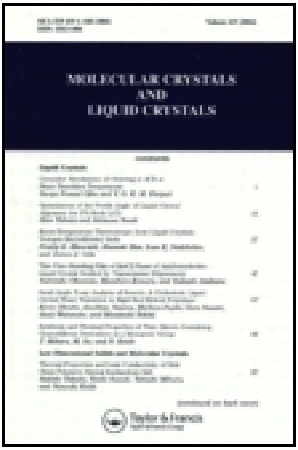

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DEUTERON MAGNETIC RESONANCE STUDY OF ORDER AND DYNAMICS IN LIQUID CRYSTAL POLYMERS

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Abstract Thermotropic nematic polyesters, specifically deuterated at different positions of the polymer chain are studied by multiple pulse dynamic NMR. Analysis of the NMR experiments is achieved, employing a comprehensive model, based on the stochastic Liouville equation. Computer simulations provide the orientational distributions and conformations of the polymer chains and the correlation times of the various motions. In the anisotropic melt the correlation times for chain reorientation and trans-gauche-isomerization are in the range of 0.1-10 ns. Decreasing the temperature of the solid polymer first freezes the intermolecular motions. Thus, below the glass transition only intramolecular motions such as trans-gauche isomerization and ring flips can be detected. The chain order parameter of the nematic melt is $S(ZZ) = 0.85$. In addition, the chains adopt a highly extended conformation, evidenced by a trans population of $n(t) \cong 0.8$ throughout the entire spacer. This microorder is retained, when the polymer is cooled below the melting point and glass transition, respectively.

INTRODUCTION

Liquid crystal polymers in which the mesogenic units exist within the polymer main chain are of considerable current interest, because of both their theoretical and technological aspects. The occurrence of thermotropic mesophases in bulk polymers presents a challenging theoretical problem.[1-3] The ease to which these polymers can be oriented has been applied to the formation of fibers with unusually high tensile strengths and moduli.[4,5] While considerable interest has centered around the synthetic design and macroscopic behaviour, relatively little attention has focused on the dynamic and structural features of the molecular units. Unknown so far are any details about molecular motion in the liquid crystal state. Moreover, there is only limited information about the microorder of the polymer chains and the alignment of the domains in electric and magnetic fields. In the present study we investigate these molecular properties with deuteron magnetic resonance (^{2}H NMR) spectroscopy, employing multiple pulse techniques.

THEORY

Multiple pulse dynamic NMR[6-8] is a time domain technique. The spin system is subject to a sequence of high power r.f. pulses and the response after the last pulse is Fourier transformed in order to obtain a frequency spectrum. According to the sequences, different NMR spectra are obtained. Moreover, significant spectral changes occur when the pulse separations are varied. Similar is true for macroscopically aligned samples at different orientations with respect to the magnetic field. Apparently, variation of typical NMR parameters such as pulse sequence, pulse separation or magnetic field orientation provides a large number of independent experiments.

Analysis of these experiments in terms of molecular order and dynamics requires a comprehensive model. We have developed such a model,[6] based on the density matrix formalism, which is schematically represented in Figure 1.

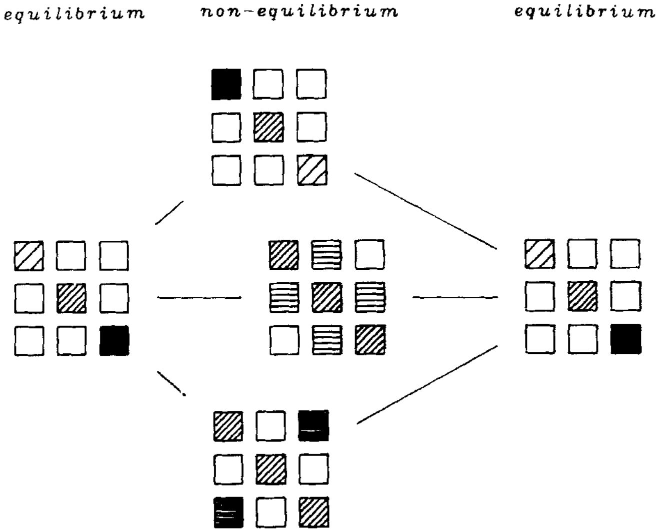

FIGURE 1. Density matrix of an I = 1 spin system, characterizing various states in multiple pulse dynamic NMR. The squares symbolize diagonal and off-diagonal matrix elements, hatched according to their populations. Equilibrium state: Boltzmann population. Non-equilibrium states: Inverted Boltzmann population (top), single quantum excitation (center), and double quantum excitation (bottom).

Before any r.f. pulse is applied, the I = 1 spin system is at thermal equilibrium. Application of the first pulse creates a defined initial state. After the pulse the density matrix evolves in time under the influence of the magnetic interactions of the spin system. Then a second pulse is applied, preparing a new initial condition and so on. After the last pulse the density matrix is Fourier transformed to yield the frequency spectrum.

The action of the different pulses on the density matrix is considered by unitary transformations, employing

Wigner rotation matrices.[6,9] Between the pulses the density matrix evolves according to the stochastic Liouville equation,[10-13] which we solve using a finite grid point method.[6] The spin Hamiltonian employed in this study considers Zeeman and quadrupole interactions of deuterons, including non-secular contributions. The equilibrium distribution of the C-D bond vectors is described by an orientational distribution function, depending on internal and external coordinates.[6] The internal part considers different conformations and the external part[14,15]

$$\begin{aligned} f(\Theta,\Psi) &= N_1 \exp[A(\cos\xi\cos\Theta - \sin\xi\sin\Theta\cos\Psi)^2] \\ \cos\xi &= \cos\delta\cos\rho - \sin\delta\cos\varepsilon\sin\rho \qquad (1) \\ f(\delta,\varepsilon) &= N_2 \exp(B\cos^2\delta) \end{aligned}$$

different orientations. Here Θ, Ψ, δ, ε, ρ are Euler angles, relating various molecular and laboratory systems.[6] The coefficient A characterizes the orientation with respect to a local director (microorder), while the parameter B specifies the orientation of the director axes in a laboratory frame (macroorder). Micro- and macroorder parameters S_{ZZ} and $S_{z''z''}$ are related to the coefficients A and B by mean value integrals[16]

$$\begin{aligned} S_{ZZ} &= \frac{1}{2} N_1 \int_0^\pi (3\cos^2\beta-1)\exp(A\cos^2\beta)\sin\beta d\beta \\ S_{z''z''} &= \frac{1}{2} N_2 \int_0^\pi (3\cos^2\delta-1)\exp(B\cos^2\delta)\sin\delta d\delta \end{aligned} \qquad (2)$$

The dynamic terms in the stochastic Liouville equation depend upon the assumption used to describe the motion. For the intermolecular motion a diffusive process is assumed (rotation through a sequence of small angular steps). In that case intermolecular reorientation can be characterized by two rotational correlation times $\tau_{R\perp}$ and $\tau_{R\parallel}$. $\tau_{R\perp}$ is the correlation time for reorientation of the symmetry axis of the molecular diffusion tensor, while $\tau_{R\parallel}$ refers to rotation about it. For the intramolecular motion a random jump process is assumed. Thus, isomerization occurs through jumps between different conformations with an average lifetime τ_J.

EXPERIMENTS AND METHODS

The family of liquid crystal polymers for this study has the general structure shown in Figure 2, in which the Roman numerals, I-V, refer to five different polymers deuterated at different sites in the repeating unit, as indicated in the formula.[17,18] The polyesters I-III exhibit a glass temperature at 303 K, a melting point at 433 K and a clearing temperature at 553 K, forming a stable nematic melt over the latter temperature range (DSC and polarization microscopy).

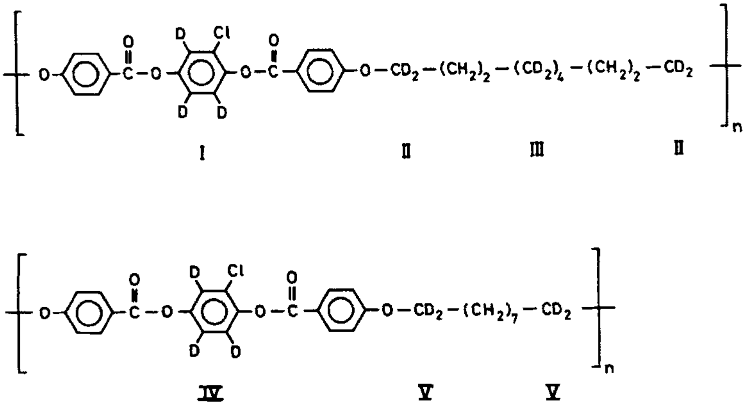

FIGURE 2. Molecular structures of the liquid crystal polyesters studied. The Roman numerals refer to five different polymers, specifically deuterated at the sites, indicated in the formula.

The nematic range of the polymers IV and V is slightly smaller, extending from 429 K to 543 K. The average molecular weight $\overline{M}_n$ of the samples varied between $3000 \leq \overline{M}_n \leq 10000$ (vapor pressure osmometry). Deuteron labels were attached either to the central phenylring (I, IV) of the mesogenic unit or to various positions (II, III, V) in the aliphatic spacer, as described elsewhere.[19] A magnetic field of 7.0 T was employed to macroscopically align the samples.[20]

The ^{2}H NMR experiments were performed on a BRUKER CXP 300 pulse spectrometer at 46.1 MHz, using inversion recovery $(180^\circ_{x'} - \tau_1 - 90^\circ_{x'} - \tau_2 - 90^\circ_{y'})$ and quadrupole echo sequences $(90^\circ_{x'} - \tau - 90^\circ_{y'})$. The width for a 90° pulse was 3.5 μs employing a home built probe, equipped with a goniometer. All experiments were recorded using quadrature detection and phase alternating sequences. The number of scans varied between 500 and 2000.

A FORTRAN programme was employed to analyze the ^{2}H NMR experiments. The programme DEUROTJUMP calculates multiple pulse NMR lineshapes of $I = 1$ spin systems undergoing inter- and intramolecular motion in an anisotropic medium.[6] The quadrupolar coupling, used in the calculations was e^2qQ/h = 165 kHz. Analysis of the ^{2}H NMR experiments requires knowledge of the molecular structure and symmetry. To proceed we assume that each molecular conformation can be approximated to a cylindrical rod, the symmetry axis of which is parallel to the long molecular axis (order tensor axis). This approximation is justified by the overall shape of the repeating unit, which is also expected to exhibit axially symmetric rotational diffusion about this axis.

RESULTS AND DISCUSSION

Macroscopically aligned samples of the liquid crystal polymers I-V were studied over a wide temperature range, using multiple pulse NMR techniques. The observed ^{2}H NMR lineshapes, varying drastically with pulse sequence, pulse separation and magnetic field orientation, were simulated, employing the NMR model outlined above. An iterative fit of several angular and pulse dependent lineshapes for any given temperature provided reliable values for the simulation parameter, i.e. the micro- and macroorder parameters, the rotational correlation times, and the lifetimes and populations of particular conformations. Generally good agreement between experimental and simulated lineshapes was found.

In Figure 3 the correlation times for the various motions of polymer II are plotted as a function of 1/T. They refer to reorientation of the long axis (full squares) and trans-gauche isomerization (open circles) of the first spacer segment, respectively. In the melt the correlation time for reorientation of the long axis is of the order of $\tau_{R\perp} = 10^{-8}$ s, while trans-gauche isomerization occurs even faster. Apparently these rapid motions are responsible for the unusual rheological behaviour of liquid crystal polymers.[5] At the melting point, within a temperature range of 20 K, all motions decrease abruptly. Lowering the temperature in the solid state first freezes all intermolecular motions. Thus, below the glass transition only intramolecular motions such as trans-gauche isomerization can be detected. In fact, isomerization of the aliphatic spacer is observed even at T = 130 K with a correlation time of $\tau_J \cong 10^{-4}$ s. The low activation energy of E_J = 6 kJ/mol for this jump process agrees with previous T_1 dispersion measurements on paraffins.[21]

Thus, the chain dynamics of liquid crystal polyesters in three different phases, including the glassy state, could be determined.

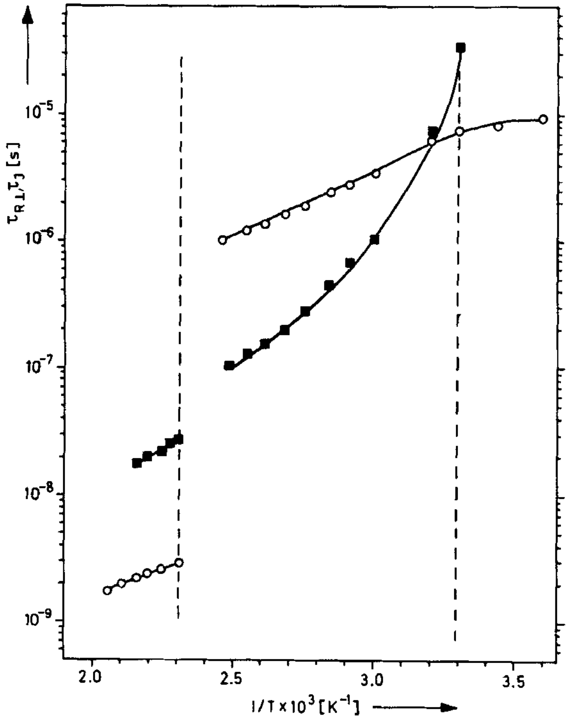

FIGURE 3. Arrhenius plot of various correlation times, characterizing the molecular dynamics of liquid crystal polyester II. Full squares refer to intermolecular motion (reorientation of the long axis) and open circles denote intramolecular motion (trans-gauche isomerization of the first spacer segment). The dashed lines indicate the melting point (T = 433 K) and glass transition (T = 303 K), respectively. The uncertainty in correlation times is generally < 10 %, except for $\tau_{R\perp}$, $\tau_J > 5 \times 10^{-4}$ s.

The microorder of the liquid crystal polyesters is conveniently discussed in terms of two parameters S_{ZZ} and n_t, characterizing the average orientation of the long molecular axis with respect to the director and the trans population of the labelled spacer segment. From the angular dependent lineshapes of polymer I the angle α between the long molecular axis and the para axis of the central ring was determined to be $\alpha = 14°$. In Figure 4 S_{ZZ} and n_t are plotted as a function of temperature. Full squares denote S_{ZZ}, while open circles refer to n_t of the outer and central spacer segments likewise (polymers II and III). One sees, that in the nematic melt $S_{ZZ} = 0.85$, a value considerably larger than those observed in low molecular weight nematogens. Thus, the polymer chains are highly ordered on a molecular level in agreement with X-ray diffraction[22,23], ESR[24], and ^{1}H NMR studies.[25,26] In addition, this work shows that the chains adopt a highly extended conformation, evidenced by a trans population of $n_t \cong 0.8$ throughout the entire spacer.

Interestingly, the order parameter S_{ZZ} is retained, when the polymer is cooled below the melting point and glass transition, respectively. Thus, in contrast to conventional liquid crystals nematic order of main chain polymers can be frozen in at the glass transition. No change in the order parameter is observed over a period of one year, keeping the sample at room temperature. In all systems studied S_{ZZ} is independent of the molecular weight of the polymers within the range $3000 \leq \overline{M}_n \leq 10000$, according to a plateau effect, observed for liquid crystal side and main chain polymers.[27-29]

So far, the discussion referred to the polyesters I-III, having ten segments in the aliphatic spacer. Reducing the spacer length to nine methylene groups causes a pronounced change of the microorder parameter S_{ZZ}. Preliminary results for the polymers IV and V, denoted by open triangles in Figure 4, indicate a significant reduction of S_{ZZ} in the anitropic melt and a further decrease at the melting point. This marked even-odd effect, also observed in other thermotropic polymers$^{30-33}$ presents a challenging theoretical problem.

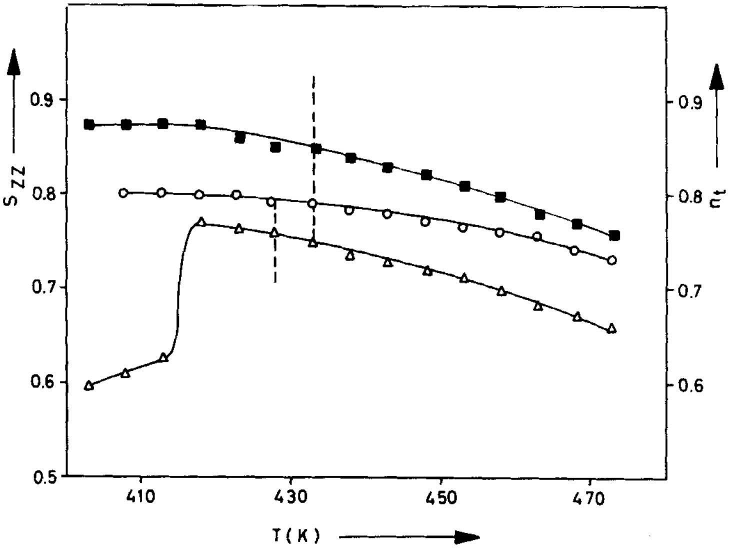

FIGURE 4. The temperature dependence of the microorder parameter S(ZZ) and trans population n(t) of the liquid crystal polyesters studied. Full squares denote S(ZZ) of polymers I-III, while open circles refer to n(t) of the outer and central spacer segments, likewise. Open triangles indicate the microorder parameters S(ZZ) of polymers IV-V, having only nine segments in the aliphatic spacer. The dashed lines denote the melting point at T = 433 K and T = 429 K, respectively. The maximum errors for S(ZZ) and n(t) are ± 4 %.

The degree of macroscopic alignment $S_{z''z''}$ of the liquid crystal polymers depends on the orientation method. Because the anisotropic permittivity of the polyester is negative, only a two-dimensional distribution of director axes was achieved using high electric fields. However, a uniform alignment of the domains was obtained by a magnetic field of 7.0 T. A detailed analysis of the angular dependent lineshapes yielded a macroorder parameter of $S_{z''z''} = 1.0$. Likewise, solid state extrusion of the liquid crystal polyester produces fibers with $S_{z''z''} = 0.9$.[24] High modulus and strengths may result from this highly oriented chain configuration. The preparation of fibers by spinning from the anisotropic melt is presently being studied.

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