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NMR-Investigations of Field Induced Orientation in Liquid-Crystalline Polymer Layers

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Solid state NMR is used to study the orientational order in thin layers of a liquid-crystalline polymer after a preceding influence of an orienting field. Samples were produced of polysiloxane with the mesogenic group in the side chain by melting the polymer between plated glass. In order to achieve a good orientation cooling has been stopped at the clearing temperature for 2 h and then carried on to room temperature with the electric and the magnetic field, respectively, still applied. Alignment of domains could be realized only in part by the electric dc field.

KEY WORDS Liquid crystal polymers, polymer layers, external fields, orientational order, nuclear magnetic resonance.

INTRODUCTION

Much attention has been focused in the recent years on thermotropic liquid-crystalline side-chain polymers which have come to prominence due to their intrinsic interest as a new class of polymers and their possible uses as optical information storage media, nonlinear optical materials, ferroelectric materials etc.^{1–7}

For a number of applications thin polymeric layers are of special interest and it has been shown that polymer films may be prepared with a random orientation of molecules or the latter can be aligned by mechanical, magnetic and electric fields.^{8–9}

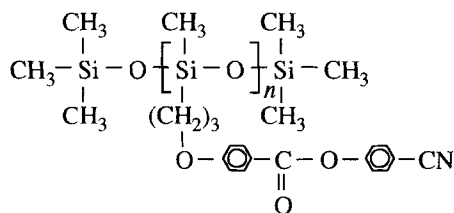
NMR, which has become a successful tool in polymer characterization, makes possible a number of ways for monitoring the degree of alignment.^{10–13}

This paper is aimed at proton NMR investigations of the orientational order in thin layers of a comb-like polysiloxane produced by a dc electric field.

EXPERIMENTAL

The special thermotropic side-chain polymer was provided by B. Krücke (Martin-Luther-Universität Halle), (see the chemical formula below).

The phase transition is known to be S_A 140 I. The polymer is characterized by a large dipole moment caused by the CN-group in the side chain.



For producing thin polymeric layers of approximately $50 \mu\text{m}$ in thickness sandwich cells made of $4 \times 20 \text{ mm}$ glass plates have been used. The glass plates had a separation by two spacers of polyimide and were covered with evaporated aluminium allowing electric poling. For this purpose the samples were heated to 150°C and a voltage of 500 V was applied. After 1 h at constant temperature the cell was cooled to 120°C with a rate of 5 K h^{-1} and a stop at T_c for several hours in order to achieve a good alignment. From 120°C down to room temperature the cooling procedure has been carried out without temperature control but with the voltage still applied. The direction of the electric field was parallel to the normal of the layer. For comparison a magnetic orienting field was used in a similar way. The temperature has been controlled as described above and the magnetic field strength applied was 2.1 T . In this case the direction of the field was perpendicular to the normal of the layer.

The NMR measurements were carried out using a Fourier-transform spectrometer of type FKS 178. In order to get a good signal-to-noise ratio 1000 scans were accumulated in each case.

ANALYSIS OF SPECTRA

Proton line shapes of oriented molecules very often show pronounced splittings, which make it possible to obtain the parameter of orientation S' .

For the simplest case of a two-proton system, the resonance spectrum is a doublet according to the orientations of a proton dipole with respect to the magnetic field B_0 .

The line splitting $\Delta\nu_{ij}$ is given by the well-known expression

$$\Delta\nu_{ij} = \frac{3}{4} \gamma^2 \frac{\hbar}{r_{ij}^3} \frac{\mu_0}{4\pi^2} (3\cos^2\Theta_{ij} - 1), \quad (1)$$

where γ is the gyromagnetic ratio of protons, \hbar is the Planck constant, r_{ij} is the internuclear vector, Θ_{ij} is the angle between r_{ij} and B_0 , $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$.

However, in reality an ensemble of two-spin systems undergoing molecular motion has to be considered and instead of Equation (1) one has to calculate

$$\langle \Delta\nu_{ij} \rangle = F \left\langle \frac{3\cos^2\Theta_{ij} - 1}{r_{ij}^3} \right\rangle \quad (2)$$

with

$$F = \frac{3}{4} \gamma^2 \hbar \frac{\mu_0}{4\pi^2}. \quad (3)$$

In Reference 13 an interpretation was given for samples with “transverse isotropy”. This means in particular

- (i) fast reorientation of the side-chain axis \mathbf{a} (no preferred direction perpendicular to \mathbf{a}),
- (ii) within a domain the axes \mathbf{a} are uniformly distributed on a cone around the director axis \mathbf{d} (described by an order parameter S),
- (iii) the director distribution is axially symmetric around a preferred axis \mathbf{D} (described by an parameter of orientational order S').

Using this assumptions and known transformation rules one gets from Equation (2)

$$\langle \Delta \nu_{ij} \rangle = 2F S_{ij} S S' S_D, \quad (4)$$

where

$$S_D = \frac{1}{2} (3\cos^2\Phi - 1) \quad (5)$$

$$S_{ij} = \frac{1}{2} \left\langle \frac{3\cos^2\vartheta_{ij} - 1}{r_{ij}^3} \right\rangle \quad (6)$$

and ϑ_{ij} is the angle between \mathbf{r}_{ij} and \mathbf{a} , Φ is the angle between \mathbf{B}_0 and \mathbf{D} (\mathbf{B}_0 , z -plane). Here S_{ij} provides information about the molecular structure (average conformation).

There are, however, uncertainties in the evaluation of the order parameter by simply measuring the splittings (in more or less resolved spectra) in cases where the line shape has a more general form.

The simulating of proton spectra is used¹⁴ which allows to determine the order parameter of phenyl rings within a liquid-crystalline side-chain polymer. It is based on the following approximations:¹⁵

- (i) only intramolecular interactions are considered,
- (ii) the calculation is based on the secular part of the Hamiltonian,
- (iii) the scalar term is neglected, leading to

$$H = -\hbar \sum_{i<j}^N b_{ij} I_{iz} I_{jz}, \quad (7)$$

where

$$b_{ij} = \frac{3}{2r_{ij}^3} \gamma^2 \hbar \frac{\mu_0}{4\pi} (3\cos^2\Theta_{ij} - 1), \quad (8)$$

I_j means the spin operator of the proton j .

In this case the corresponding line shape $F(\omega)$ is the superposition of $N2^{N-1}$ δ -functions

$$F(\omega) = \frac{1}{N2^{N-1}} \sum_{i=1}^N \sum_{m_k} \delta(\omega - \omega_{i,m_k}) \quad (9)$$

with $m_k = \pm 1/2$ and ω_{i,m_k} is given by

$$\omega_{i,m_k} = \sum_{i \neq j} b_{ij} m_j. \quad (10)$$

Because of the molecular motion one has to average the frequencies b_{ij} over a time interval of order T_2 (free induction decay time of a solid). To evaluate \bar{b}_{ij} it is convenient to separate intramolecular motion (CH_3 group rotation, phenyl ring flips, conformational changes) from the motion of the molecule as a whole and similar to Equation (4) one gets

$$\bar{b}_{ij} = \frac{3}{2} \gamma^2 \hbar \frac{\mu_0}{4\pi} S_{ij} S S' (3\cos^2\Phi - 1). \quad (11)$$

If a molecule remains rigid during its motion the conformation parameter S_{ij} has the value corresponding to its fixed geometry

$$S_{ij} = S_{ij}^0 = \left[\frac{1}{2r_{ij}^3} (3\cos^2\vartheta_{ij} - 1) \right]_0. \quad (12)$$

If there are fast intramolecular motions of the protons, e.g. n jumps between p different positions, S_{ij} is the arithmetic mean

$$S_{ij} = \frac{1}{n} \sum_{p=1}^n S_p^{ij}. \quad (13)$$

Equation (13) applies, for instance, in the case of 180° flips around the phenyl para-axis or 120° methyl group jumps around a C_3 axis. In a more complicated case of intramolecular motion the time average of S_{ij} may be described by

$$S_{ij} = S_{ij}^0 S_i S_j, \quad (14)$$

where the S_i are phenomenological conformation parameters. The product $S_i S_j$ has the meaning of an order parameter of the internuclear vector \mathbf{r}_{ij} within the molecular frame.

The line shape simulations were carried out in three steps. At first the spectrum has been calculated by a superposition of about 10^6 δ -functions including all protons of one monomer unit. Secondly, different mobilities of molecular groups in the side chain (methylene groups, benzene rings) and in the main chain (methyl group) were considered by introducing the parameters S_1 , S_2 , S_3 (see above). In addition, intermolecular effects have been taken into account qualitatively by a convolution of the calculated spectrum by a Lorentzian line of 2 kHz in width.

RESULTS AND DISCUSSION

Spectra of the sample investigated show typical features of proton line shapes (see Figure 1).

The major part of the signals is caused by the protons of the mesogenic units and the central component is interpreted as to be due to the nuclei in the mobile methyl groups. According to the temperature applied during the measurements the linewidths of the resonance lines are in the range of 5–7 kHz. Figure 2 shows the angular dependence of the halfwidths. The angular dependence of linewidths measured at 20% of the maximum magnitude is more pronounced, showing a minimum at $\Phi \approx 54^\circ$.

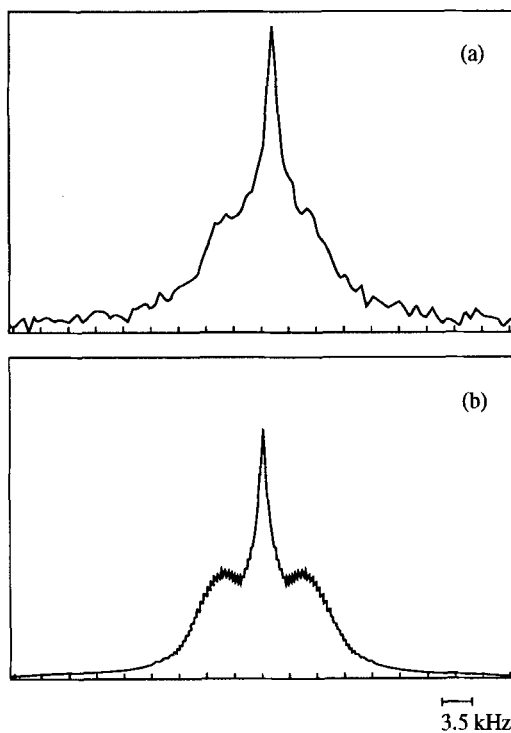


FIGURE 1 ^1H -NMR spectra (a) measured at $\Phi = 90^\circ$ after poling and (b) calculated for $\Phi = 90^\circ$.

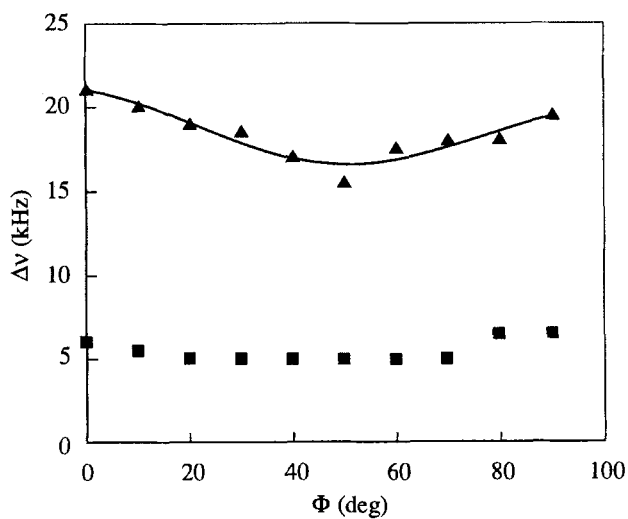


FIGURE 2 Angular dependence of the linewidth measured after poling at 50% (▲) and 20% (■) of maximum line magnitude.

In order to interpret the experimental results, an angle of 10° between the side-chain axis and the para-axis of the benzene rings, and a value $\langle r_{ij} \rangle = 2.45 \text{ \AA}$ for the internuclear

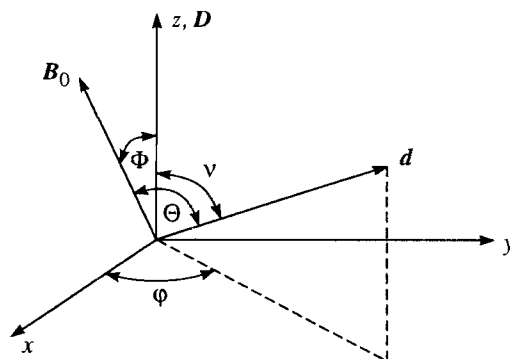


FIGURE 3 Orientation of director d within the laboratory frame x, y, z . ψ, φ are Euler angles of d ; Φ is the angle between B_0 and D (B_0, z -plane); Θ is the angle between B_0 and d .

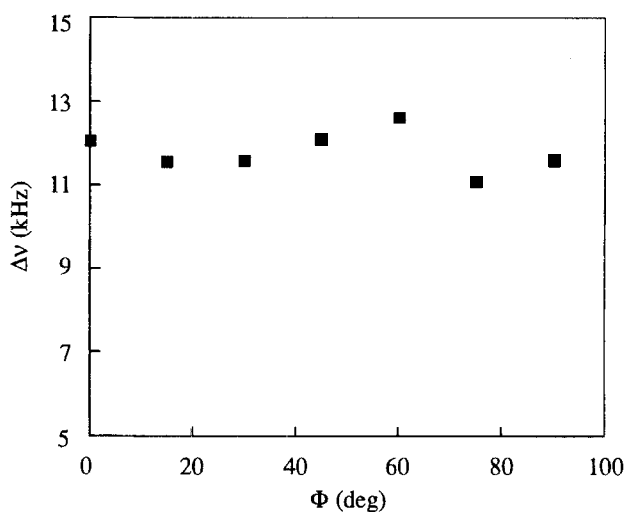


FIGURE 4 Angular dependence of the linewidth at 50% of maximum amplitude after treatment with the external magnetic field.

distance between ortho-protons have been used. In addition an order parameter $S = 0.88$ as typical for smectic systems was assumed. As a result, the parameter of orientational order S' could be determined from the line splittings. It appeared to be equal to 0.61.

Using the above mentioned fitting procedure the best agreement with the experimental spectra was obtained at $\Phi = 90^\circ$ with $S_1 = 0.6$, $S_2 = 0.9$, and $S_3 = 0.3$ (Figure 1b).

In order to explain the incomplete orientation in the LCP layer (the directors d are distributed around a preferred direction D) the following distribution function was introduced

$$P(\vartheta) \propto \exp(\beta \cos^2 \vartheta) \quad (15)$$

leading to

$$S'_D = \frac{1}{2}(3\cos^2\Theta_D - 1)$$

$$S_D^l = \frac{1}{2} \int_0^{\pi} (3\cos^2\vartheta - 1) P(\vartheta) \sin\vartheta d\vartheta. \quad (16)$$

The parameter β corresponds to the deviation of the directors from the axis D . A good agreement with the experimental spectra could be achieved with $\beta = 4$. With this value the function $\sin\vartheta \exp(\beta \cos^2\vartheta)$ plotted in the interval $(0, \pi/2)$ has a maximum at $\vartheta = 20.5^\circ$ which is the mean deviation of the domains with respect to the preferred direction of the sample. Using Equation (16) one obtains $S' = 0.81$, which is in good agreement with the experimental results.

As shown in Figure 4 no angular dependence of the halfwidth could be obtained for the sample treated with the magnetic field. Measurements of the linewidths at 20% of the maximum amplitude did not yield further information.

In conclusion it is possible to claim that by means of a dc electric field a partial orientation of domains could be achieved in a sample containing a CN-group at the end of the side chain in contrast to a magnetic field whereby no effect of alignment could be detected.

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