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M. Winkler[a]; D. Geschke[a]; P. Holstein[a]
[a] Universität Leipzig, Fachbereich Physik, Leipzig, Germany

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Orientational behaviour of a liquid crystalline side chain polymer in applied electric and magnetic fields as detected by NMR

by M. WINKLER*, D. GESCHKE and P. HOLSTEIN
Universität Leipzig, Fachbereich Physik, Abt. Polymerphysik,
Linnéstrasse 5, D-04103 Leipzig, Germany

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The molecular orientational order of a side chain thermotropic nematic polymer has been measured by proton NMR. The alignment of the side chains is reflected in the splitting of the NMR signal into a doublet. Simultaneous orientational effects of magnetic and electric fields on the mesogenic groups were studied in magnetically preoriented layers. Temperature, twist angle and thickness dependences of the spectra were measured. The order parameter S and the parameter of orientational order S' of the samples were estimated.

1. Introduction

Thermotropic liquid crystalline side chain polymers (LCPs) have come to prominence in recent years due to their intrinsic interest as a new class of polymer and their possible uses as optical information storage media and non-linear optical materials.

LCPs are combine the electroactive and magnetoactive properties of low molar mass mesogens with the properties of macromolecules. They are homeotropically oriented when exposed to an appropriate external field and the alignment is capable of being frozen into the solid state. For most applications, a macroscopically oriented domain over a large area has to be prepared. To obtain the desired effects preoriented samples are then exposed to external fields. From the practical point of view, in the case of optical storage or display devices, thin layers of liquid crystalline polymers are of special importance.

In this contribution we report results of proton NMR studies of an orientational parameter in thin layers that were obtained by alignment of the mesogenic units using magnetic and electric fields.

2. Theoretical

The model used here is valid for the Fréedericksz transition by deforming the planar cell [1]. In general, the Frank free energy G_{elast} of the nematic liquid crystal is given by the well-known expression

$$G_{\mathrm{elast}} = \frac{1}{2}\int_V (K_{11}(\operatorname{div}\mathbf{n})^2 + K_{22}(\mathbf{n}\operatorname{rot}\mathbf{n})_2 + K_{33}(\mathbf{n}\times\operatorname{rot}\mathbf{n})^2)\,dv, \qquad (1)$$

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* Author for correspondence.

K_{11}, K_{22} and K_{33} are the splay, twist and bend elastic constants, respectively, and v is the space coordinate of the volume V. The elastic free energy in the planar cell can be expressed as

$$G_{\text{elast}}=\frac{1}{2}\int_0^d K_{11}(\operatorname{div}\mathbf{n})^2\,dz=\frac{1}{2}\int_0^d K_{11}\left(\frac{\partial\varphi}{\partial z}\right)^2 dz. \tag{2}$$

In the case of an additional electric field, the dielectric contribution to the free energy is

$$G_{\text{dielect}}=\frac{1}{2}\int_V \mathbf{D}\cdot\mathbf{E}\cdot dv, \tag{3}$$

where the dielectric displacement is $\mathbf{D}$ and the electric field $\mathbf{E}$. The anisotropy of the dielectric properties of the liquid crystal is given by

$$\Delta\varepsilon=\varepsilon_{\|}-\varepsilon_{\perp}, \tag{4}$$

where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the optical axis, respectively. Now the dielectric free energy is

$$G_{\text{dielect}}=\frac{1}{2}\int_0^d -\varepsilon_0\Delta\varepsilon(\mathbf{E}\cdot\mathbf{n})^2\,dz. \tag{5}$$

The density of the director field in the sample is given by

$$G=\frac{1}{2}\int_0^d\left[K_{11}\left(\frac{\partial\varphi}{\partial z}\right)^2-\varepsilon_0\Delta\varepsilon E^2\sin^2\theta\right]dv, \tag{6}$$

where the vacuum permittivity is ε_0 and the angle θ is that between the director $\mathbf{n}$ and the initial orientation. According to equation (6), it is possible to calculate the state of deformation of the director field $\theta(z)$ by minimizing the free energy density per unit area. By setting electric energy equal to field energy and solving the differential equation under the conditions $\theta(0)=0$ and $\theta(d)=0$, we get, for a small deviation $\theta(d/2)=0_{\mathrm{m}}$ in the middle of the cell,

$$E=E_0(1+\tfrac{1}{4}\sin^2\theta_{\mathrm{m}}+\cdots), \tag{7}$$

with the threshold field strength

$$E_0=\frac{\pi}{d}\sqrt{\left(\frac{K_{11}}{\varepsilon_0|\Delta\varepsilon|}\right)}.$$

The NMR resonance line is, for the simplest case of a two-proton system, a doublet according to the two orientations of a proton dipole in the $\mathbf{B}_0$ field. From the dipolar splitting it is possible to obtain, to a good approximation, the order of parameter S_{zz}, since the most ordered molecular axis is close to the *para*-axis. The dipolar splitting is given by

$$\Delta\nu=\frac{3\mu_0}{16\pi^2}\frac{\gamma^2\hbar}{\langle\mathbf{r}\rangle^3}S_{ij}R_{ij}, \tag{8}$$

where $\mu_0=4\pi\cdot10^{-7}$ Vs/(Am), the gyromagnetic ratio of protons is γ and $\hbar$ is Planck's constant divided by 2π. S_{ij} is an element of the Saupe order tensor, R_{ij} is a conformation dependent tensor element and **r** is the internuclear vector. In the principal frame of S_{ij} the dipolar splitting becomes

$$\Delta\nu = \frac{3\mu_0}{16\pi^2}\frac{\gamma^2\hbar}{\langle r\rangle^3}\left[S_{ZZ}R_{ZZ} + \tfrac{1}{3}(S_{XX} - S_{YY})(R_{XX} - R_{YY})\right], \tag{9}$$

with

$$R_{ZZ} = \tfrac{3}{2}\cos^2\Phi - \tfrac{1}{2} \quad \text{and} \quad R_{XX} - R_{YY} = \tfrac{3}{2}\sin^2\Phi\cos 2\alpha,$$

where Φ is the angle between the most ordered molecular axis and the *para*-axis of the benzene rings. $R_{XX} - R_{YY}$ is directly associated with the distribution of the eulerian angle α that characterizes the azimuth of the orientation of the side-chain axis. The angle Φ has a value not larger than 10 degrees. In this situation $(S_{XX} - S_{YY})(R_{XX} - R_{YY})$ is negligible compared to $S_{ZZ}R_{ZZ}$ [2]. Therefore S_{ZZ} can be obtained from the dipolar splitting or from the ϕ-angle dependence of the line-width [3] (ϕ is the angle between $\mathbf{B}_0$ and a preferred axis in the sample).

An interpretation is given here only for samples with transverse isotropy. This means in particular

fast reorientation of the side chain axis,

within the domain, the side-chain axes are uniformly distributed on a cone around the director axes,

the director distribution is axially symmetric around a preferred axis in the sample.

In consideration of this, S_{ZZ} can be replaced by $S\cdot S'$. The line splitting of the NMR signal of sample with transverse isotropy shows dependences on the order parameter S within the domain and on the orientational order parameter S' of the domain referring to the preferred axis in the sample.

$$\Delta\nu = \frac{3\mu_0}{16\pi^2}\frac{\gamma^2\hbar}{\langle \mathbf{r}\rangle^3}\cdot\tfrac{1}{2}(3\cos^2\phi - 1)\cdot S\cdot S'. \tag{10}$$

3. Experimental

The material investigated here is a side chain thermotropic polyacrylate with the structure shown in figure 1. It was distributed by Industrial Chemicals Division of Merck Ltd, UK, and was first described by Le Barny *et al.* [4].

The thermal behaviour of the polymer was investigated using a polarizing microscope, Amplival Pol-U (Carl Zeiss Jena) with a heating stage. The polymer forms an isotropic phase above the clearing point at $T_{NI} = 130°C$ and a nematic threaded texture between T_{NI} and the glass transition at $T_g = 32°C$.

The substance was contained in sandwich cells (see figure 2) made from In_2O_3/SnO_2.

ITO-coated glass separated by polyimide spacers in the range 20–500 μm. The glass surfaces were cleaned, but not further treated.

The layer thickness used in the cells is a compromise between the minimal thickness to achieve a sufficient sample signal and a maximal size to obtain the necessary electric field strength. The cell is filled over some hours by capillary action, while the sample is kept 20 degrees above the clearing point. An isotropic texture in the cells was checked by polarizing microscopy and proton NMR before applying the orientational procedure. A field strength between 0·005 and 1 MV m^{-1} was used. Short circuits in the cell can

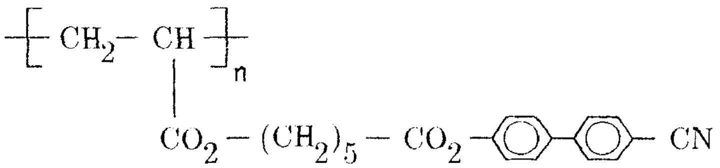

Figure 1. Structure of the polymer LCP105, $M_n = 4880$, $M_w = 8030$, $M_w/M_n = 1{\cdot}64$, average $n = 13{\cdot}5$ units.

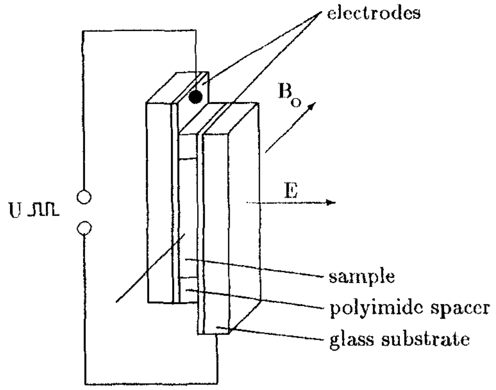

Figure 2. Sample geometry in the spectrometer.

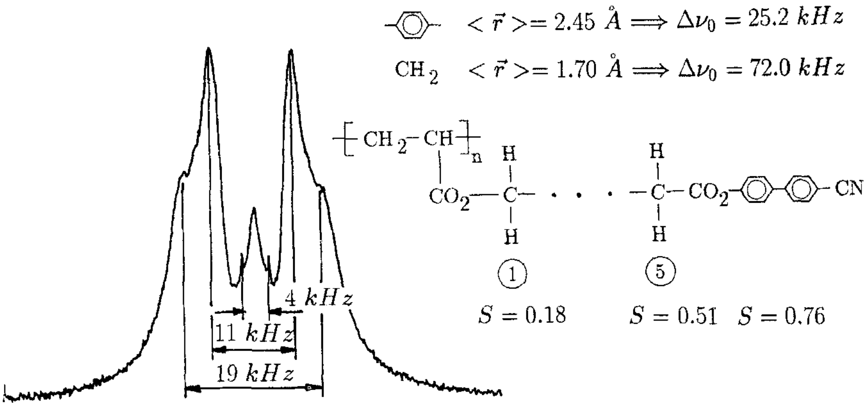

Figure 3. Order parameters S of a bulk sample in the nematic phase, $T = 110°\mathrm{C}$, $B_0 = 1{\cdot}4\,\mathrm{T}$.

occur at higher field strengths. The NMR spectra were obtained with a Bruker MSL 500 spectrometer working at 500 MHz (11·7 T) and a FKS 178 spectrometer operating at 60 MHz (1·4 T) for protons. 50–8000 scans were accumulated for each spectrum to achieve signal-to-noise ratio.

4. Results and discussion

The influence of the applied electric field (shape, amplitude and frequency), of the magnetic field and of temperature on the orientational behaviour was studied. Some representative results will be discussed.

4.1. *Magnetic alignment*

In a liquid crystal with positive magnetic anisotropy $\Delta\chi$, the director tends to align parallel to an external magnetic field $\mathbf{B}_0$ [5]. The orientation of a bulk sample in a NMR tube (5 mm o.d.) under the influence of the spectrometer magnetic field ($\mathbf{B}_0$ field) produced well-oriented samples (see figure 3).

The alignment of the rigid side chains along the $\mathbf{B}_0$ direction has its origin in the anisotropic diamagnetic susceptibility ($\Delta\chi \approx 10^{-9}\,\mathrm{m}^3\,\mathrm{kg}^{-1}$) mainly due to the biphenyl groups [6, 7].

The spectra are dominated by the dipolar interaction between the *ortho*-protons of each benzene ring. The line splitting in the 11·7 T field is the same as in the 1·4 T field, because the sample is perfectly aligned (cf. figure 5 and figure 6). The orientational order parameter S' is near to 1. In this case, it is possible to describe the order parameter S of different protons in the material by using equation (10). In order to interpret the experimental results (see figure 3) an angle of 10° between the side-chain axis and the *para*-axis of the benzene rings and a value $\langle \mathbf{r} \rangle = 2{\cdot}45\,\text{Å}$ for the internuclear distance between the *ortho*-protons have been used. In addition, a value of $\langle \mathbf{r} \rangle = 1{\cdot}70\,\text{Å}$ between the protons of the CH_2-groups and an angle of 90° between the side chain axis and this internuclear vector were assumed. The temperature dependence of the dipolar splitting of the biphenyl protons is shown in figure 5 and figure 6. The temperature dependence of the order parameter is also given there. The glass transition and the melting point are clearly indicated.

Typical proton spectra of the nematic phase of polymer LCP 105 with different layer thicknesses are presented in figure 4. Both the line splitting and the orientational order parameter S' are the same in layers from 20 μm up to the bulk sample, under the assumption of the thickness independence of the order parameter S in the domain. The sharp central line in the spectra corresponds to the isotropic component (N + I biphase) [6] and is increased with decreasing layer thickness. Also we have found a typical thickness dependence of the line-width in unoriented layers. This results suggests a thickness dependence of molecular motions in liquid crystalline polymer layers up to 500 μm.

Oriented layers stable over a long period were prepared by cooling down the sample in the strong $\mathbf{B}_0$ field to below the glass temperature. Figure 7 shows the angular dependence of the line-width of a bulk sample oriented in a magnetic field ($B_0 = 1{\cdot}4\,\mathrm{T}$) and measured at room temperature. The angular dependence of the line-width measured at 10 per cent of the maximum magnitude is more pronounced, showing a maximum at $\phi = 0°$ and a minimum at $\phi = 54°$. This indicates that in our samples the director is randomly oriented in a cone about the $\mathbf{B}_0$ field.

4.2. *Electric alignment*

By means of a strong electric field, well-oriented layers with a remarkable angular dependence of the line-width could be produced. The magnetic field influence (1·4 T) is negligible on application of an electric field higher than $E = 0{\cdot}4\,\mathrm{MV\,m}^{-1}$. Figure 8 shows the typical ($3\cos^2\phi - 1$)-dependence of the 10 per cent line-width of a 200 μm thick sample in the nematic phase in a pulsating electric field of $E = 0{\cdot}75\,\mathrm{MV\,m}^{-1}$ (ϕ describes the angle between the $\mathbf{E}$ field and the $\mathbf{B}_0$ field). The dielectric anisotropy $\Delta\varepsilon$ is positive, and therefore the director tends to align parallel to the external electric field [9].

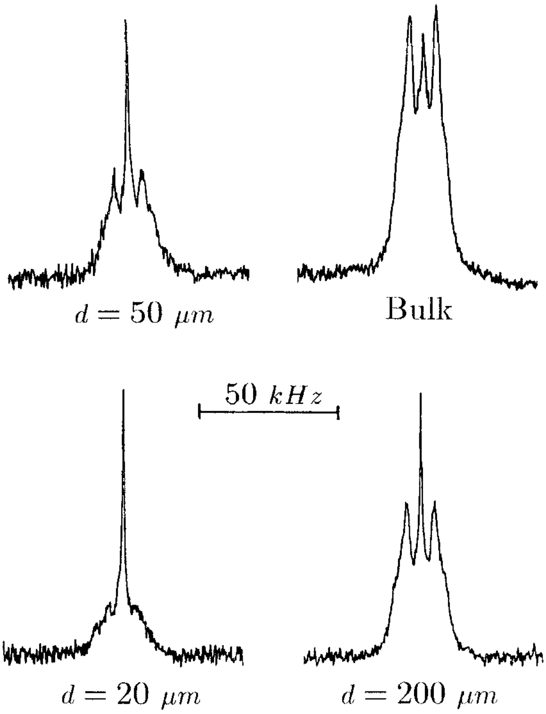

Figure 4. Thickness dependence of the spectra at 110°C, $B_0 = 1{\cdot}4\,\text{T}$.

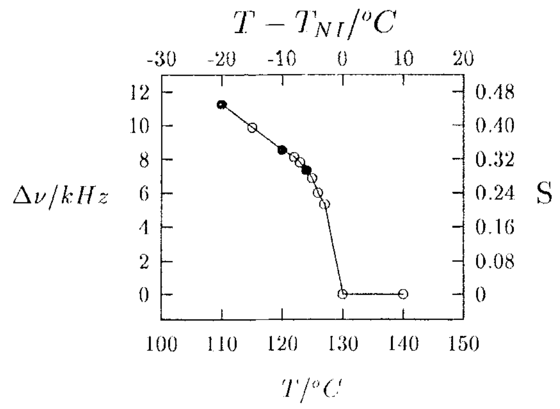

Figure 5. Temperature dependence of the dipolar splitting $\Delta\nu$ and of the order parameter S of the biphenyl protons near the N − I transition, (○) $B_0 = 1{\cdot}4\,\text{T}$, (●) $B_0 = 11{\cdot}7\,\text{T}$.

4.3. *Electrically induced Freedericksz transition in magnetically preoriented layers*

The experiments were carried out as follows:

The layer normal of the planar cell is arranged perpendicular to the strong magnetic B_0 field. A well-oriented sample was produced in the nematic phase of the polymer. The axes of the mesogenic units are arranged in the plane of the planar cell, along the magnetic field direction.

Perpendicular to the $\mathbf{B}_0$ field direction, an electric field was applied.

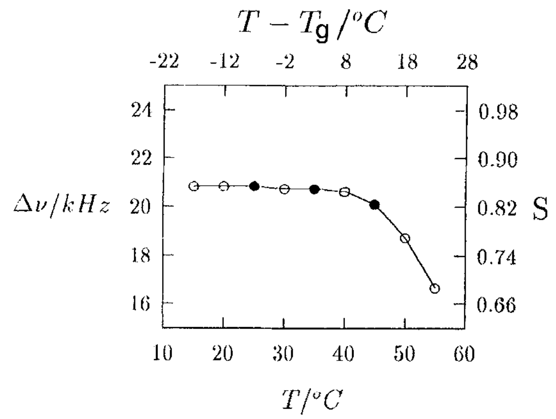

Figure 6. Temperature dependence of the dipolar spitting Δν and of the order parameter *S* of the biphenyl protons near the glass transition, (○) $B_0 = 1{\cdot}4\,\text{T}$, (●) $B_0 = 11{\cdot}7\,\text{T}$.

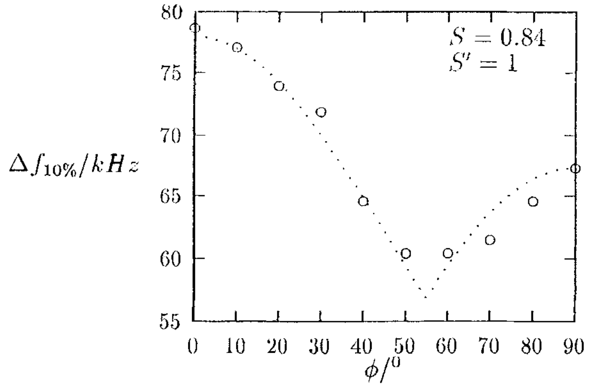

Figure 7. Angular dependence of the line-width measured at 10 per cent of maximum amplitude of a bulk sample in the glass state ($T = 30$°C), oriented at $T = 120$°C, $B_0 = 1{\cdot}4\,\text{T}$.

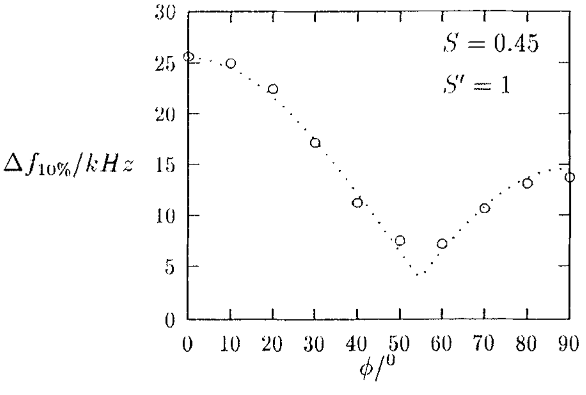

Figure 8. Angular dependence of the line-width measured at 10 per cent of maximum amplitude of a 200 μm thick sample, $T = 110$°C, $B_0 = 1{\cdot}4\,\text{T}$, $U + 150\,\text{V}$ pulsating current, $f = 100\text{Hz}$.

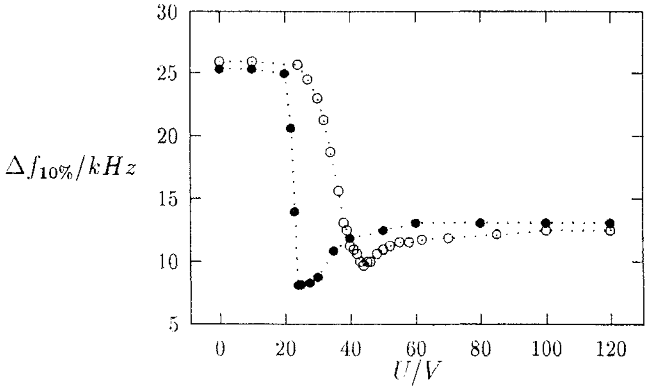

Figure 9. Voltage dependence of the line-width measured at 10 per cent of maximum amplitude of a 200 μm thick sample, $T = 110°C$, $B_0 = 1{\cdot}4\,T$, $f = 100Hz$, (○) pulsating field, (●) alternating field.

In the case it is possible to align the mesogenic units in different directions between the $\mathbf{B}_0$ and the **E** field in the case of *in situ* orientational measurements (equilibrium of electric and magnetic induced rotational moment). The alignment of the side chains towards the electric field can be switched reversibly. This is in accordance with the fact that the director field relaxes to the $\mathbf{B}_0$ direction when the **E** field is switched off. A threshold voltage of 20 V was measured. The electric field dependence of the line width of a sample is given in figure 9.

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