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ORIGINAL CONTRIBUTION

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Ordering in a nematic side-chain polymer. A proton and deuterium nuclear magnetic resonance study

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Abstract The aim of this work is to study in detail the orientational structure of liquid-crystalline polymers with different molecular weight. The advantage of our approach is the use of broad-band ^{1}H and ^{2}H NMR spectroscopy for the analysis of the orientational order of the main-chain and mesogenic groups in conjunction with small-angle neutron scattering results. Investigations of a series of partially deuterated side-chain polymers with methoxybenzylbenzoate mesogenic groups have been carried out. The deuteration of the main chain enables separate access to order and orientation effects of the side chain and the main chain. The molecular orientation of the substances investigated can be frozen in its nematic phase below the glass-transition temperature. It is independent of the molecular weight, whereas the dynamics of the director reorientation (rotational viscosity) in the nematic phase strongly depends on the molecular weight. The main-chain deuterons provide powder spectra after orientation of the polymer in magnetic fields, indicating a very weak or lacking orientational anisotropy. A complete decoupling of the main and the side group can be deduced.

Key words ^{1}H and ^{2}H nuclear magnetic resonance · Orientational dynamics · Side-chain liquid-crystalline polymer · Main-chain behaviour

Introduction

In recent years NMR techniques have been successfully used to study orientational order in liquid-crystalline side-chain polymers [1–8], whereby much interest has been focused on the main-chain parts of the molecules as well as on side-chain units close to the backbone. The ^{2}H NMR technique is known to be extremely sensitive to anisotropy effects and motions on the molecular level. It is possible to obtain detailed information by means of site-specific deuteration, which is often superior to data obtained from ^{1}H NMR studies. The objective of this work is to study the orientational order and the reorientation dynamics of a nematic liquid-crystalline polymer with different molecular weight by ^{1}H and ^{2}H NMR. The partial deuteration enables the separate investigation of main-chain (deuterated) and side-chain (remaining protons) effects. We are particularly interested in

1. The study of the order parameter, S, of the mesogenic groups of liquid-crystalline polymers P1 using broad-band ^{1}H NMR spectroscopy.
2. The investigation of the orientation of the polymer chain in the magnetic field by ^{2}H NMR spectroscopy.
3. The study of the director reorientation of different fractions of a comb-shaped liquid-crystalline polymer P1 in the magnetic field and the determination of the rotational viscosity coefficient, γ_1.
4. The investigation of the influence of the temperature and the molecular weight of the polymer P1 on S and γ_1.

^{1}H NMR has the advantage of high sensitivity; however, the superposition of the strong dipolar interaction of many protons within each molecule and between adjacent chains often provides unresolved spectra [6, 9, 10]. In contrast, ^{2}H NMR spectra are extremely sensitive to orientation and molecular mobility on the deuterated sites. Particularly, ^{2}H 2D-exchange spectroscopy gives detailed information about molecular motion [1].

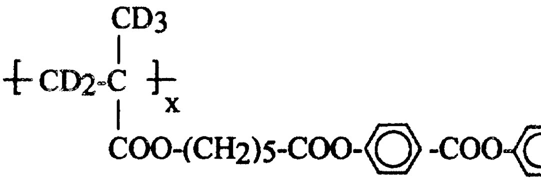
Recently developed multidimensional ^{13}C NMR–cross polarization magic-angle spinning techniques [11] give access to site-resolved molecular anisotropy in liquid-crystalline polymers. The application of rotor-synchronized data acquisition collecting 2D or 3D data allows the measurement of the order parameters for each resolvable carbon site as demonstrated, for example, for a frozen smectic liquid-crystalline side-chain polymer [12] for which it has been proved that the orientational degree for the sites in the mesogenic part of the molecule is higher than for the spacer carbons, whereas the main-chain site remains disordered. The properties of the main chain in liquid-crystalline side-chain polymers have also been reported [3].

Experimental

The materials investigated were partially deuterated polyacrylates with different molar masses (Table 1).

Polymer P1 was obtained [13, 14] by copolymerization of the corresponding monomer in absolute toluene. 2,2′ Azobis(isobutyronitrile) was used as an initiating agent. According to NMR spectroscopy, the degree of deuteration was 99.0 ± 0.2%. The as-synthesized copolymers were purified by repeated precipitation from tetrahydrofuran solutions by hexane. The polymer P1 was fractionated by precipitation (toluene was used as a solvent and ethanol as a nonsolvent). The molecular weights were estimated by gel permeation chromatography.

The chemical formula of the polymer studied in this work is given in Scheme 1.



Scheme 1 The chemical structure of polymer P1-26, −55, 154, −287

Table 1 Molecular mass characteristics, phase transitions and anisotropies of the polymer chain ($a = R_\perp/R_\parallel$) [13] of the comb-shaped liquid-crystalline polymethacrylate P1

Sample no.	Degree of polymerization, z	Phase transitions (°C)	a ($R_\perp/R_\parallel$)
P1-26	26	Glass 34 N 94 I	0.91 ± 0.27
P1-55	55	Glass 33 N 108 I	1.14 ± 0.09
P1-154	154	Glass 32 N 106 I	1.08 ± 0.05
P1-287	287	Glass 33 N 107 I	1.12 ± 0.03
Nonfractionated		Glass 33 N 103 I	

Phase transitions in the synthesized copolymers were studied by differential scanning calorimetry with a scanning rate of 10 K/min. All experiments were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarization microscope. The small-angle neutron scattering (SANS) from deuterated samples of liquid-crystalline side-chain polymers was used to determine the degree of polymerization, z, (Table 1) [15, 16] and the anisotropy a of the polymer chain. It was found that the polymer has a very weak anisotropy of the polymer chain ($a = R_\perp/R_\parallel$), where $R_\parallel$ and $R_\perp$ are the components of the radius of gyration of the polymer chain parallel and perpendicular to the director, respectively.

NMR experiments were performed using a 60 MHz spectrometer and an MSL300 operating at 300 MHz proton frequency. In order to study the behaviour of the main chain the deuterium resonance facility of an MSL300 (46 MHz) was used; this is equipped with a static double resonance probe. The probe could be tuned simultaneously to proton and deuterium frequencies and allowed a fast change of the channels and proton and deuterium experiments under identical conditions. Additionally, this probe has a laboratory-built goniometer allowing a comfortable and fast change of the angle between the sample and the static magnetic field, $\mathbf{B}_0$, during the experiment. The goniometer parts close to the coil are made from polyimide and provide no background signal for the proton investigations. All spectra were acquired by standard echo techniques (90_x-τ-90_y-τ-acq.). Experimental parameters were 10 μs echo delay for protons and 20 μs for deuterons and 1.0 μs (60 MHz), 3 μs (300 MHz) and 3 μs (46 MHz) $\pi/2$-pulse duration. The sampling rate for the ^{2}H free induction decays was 1 μs. The sample–goniometer system for the horizontally arranged NMR coil is illustrated in Fig. 1.

The construction for the sample container prevents bubbles in the liquid-crystalline or liquid phase, which is important to avoid macroscopic flow in flip experiments, which would provide inaccurate access to orientational states and to the rotational viscosities and enables experiments to be performed with only a little material. The coil in the 60 MHz spectrometer has a vertical arrangement so that changes of angles are simple.

The reorientational dynamics [10] can be described by a differential equation of the form

$$\sigma\frac{\mathrm{d}^2\Phi}{\mathrm{d}t^2}+\gamma_1\frac{\mathrm{d}\Phi}{\mathrm{d}t}-\frac{1}{2}\frac{\Delta\chi}{\mu_0}\mathbf{B}^2\sin(2\Phi-2\alpha)=0\ . \qquad (1)$$

σ is a “rotational inertia” and can be neglected. γ_1 is the rotational viscosity. $\Delta\chi$ means the anisotropy of the diamagnetic susceptibility. α denotes the start angle (deviation of the director orientation from $\mathbf{B}_0$). The angle Φ can be estimated, for example, from the splitting features in dipolar spectra, where Φ means the angle between d and $\mathbf{B}_0$. The time behaviour can be discussed with a equation of the type

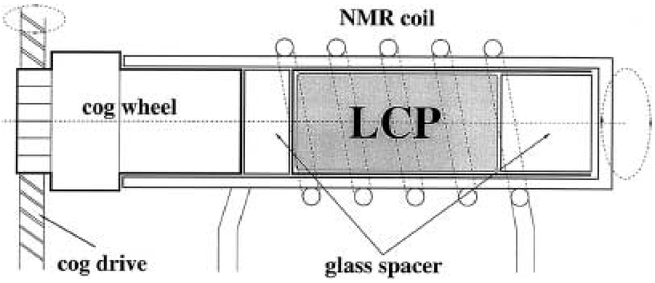


Fig. 1 The sample arrangement enables a change of the angle between the magnetic field and a preferred orientation, which was achieved by the orientation process in the nematic phase, by means of a goniometer. *LCP* represents the liquid-crystalline polymer

$$\tan[\alpha - \Phi(t)] = \tan\alpha \exp\left(-\frac{t}{\tau_\eta}\right) \ , \tag{2}$$

with the time constant

$$\tau_\eta = \frac{\gamma_1 \mu_0}{\Delta\chi \mathbf{B}_0^2} \ . \tag{3}$$

It is known that for angles $\alpha \approx \pi/2$ the reorientation can be faster (and more complicated) and does not follow Eq. (2) . In this case, γ_1 must be replaced by an effective viscosity, γ_{eff}, which is smaller.

In the case of ^{1}H NMR resonance the dipolar splitting is given by

$$\Delta\nu_{ij} = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{r_{ij}^3} \frac{1}{2} (3\cos^2\theta_{ij} - 1) \ , \tag{4}$$

with the magnetic constant μ_0, the gyromagnetic ratio of protons γ, the absolute value of an internuclear vector $\mathbf{r}_{ij}$ and Planck's constant $\hbar$, divided by 2π. θ_{ij} means the angle between $\mathbf{r}_{ij}$ and $\mathbf{B}_0$.

For the interpretation of our results we use the uniaxial phase model of transverse isotropy, i.e. there is an isotropic reorientation of the mesogenic units around the side-chain axes which are distributed on a cone around the average director axis, *d*.

Under this assumption one gets from Eq. (4)

$$\Delta\nu = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{\langle \mathbf{r}^3 \rangle} \frac{1}{2} (3\cos^2\Phi - 1) S \ , \tag{5}$$

where S is the order parameter with $S = 1$ for perfect orientation and $S = 0$ in case of isotropic distribution. In case of quadrupolar interaction of deuterons one gets for the line splitting

$$\Delta\nu_Q = \frac{3}{4} \frac{e^2 qQ}{h} [(3\cos^2\Theta - 1) + \eta \sin^2\Theta \cos 2\psi] \ . \tag{6}$$

Θ and ψ denote the polar angles. Θ is the angle between the C–D bonds and $\mathbf{B}_0$. η is an asymmetry factor, where $\eta = (V_{yy} - V_{xx})/V_{zz}$, with z being the main axis of the uniaxial electric field gradient tensor. e is the elementary charge, eq is the electric field gradient, $q = 1/e \ V_{zz}$, $V_{zz} = \partial^2 V / \partial z^2$, V is the electric potential at the nucleus and Q is the electric quadrupole moment.

For aliphatic and even for aromatic deuterons in bonds of solid materials $V_{xx} = V_{yy}$ holds and one obtains for the uniaxial phase model

$$\Delta\nu_Q = \frac{3}{4} \frac{e^2 qQ}{h} (3\cos^2\Phi - 1) S \ , \tag{7}$$

where Φ (as in Eq. 5) is the angle between the director orientation d and $\mathbf{B}_0$.

For aliphatic C–D bonds a value of e^2qQ/h = 167 kHz is known from the literature. The powder spectrum, which is a superposition of all possible orientations, Θ, is extremely sensitive to molecular motions on a segmental level. For aliphatic C–D bonds a splitting of the pronounced singularities in the powder spectrum of the order of 125–127 kHz [17] is expected. For rotating methyl groups the splitting is scaled by a factor of 1/3.

Averaging of the molecular motion should influence the local order parameters of the mesogenic group, of the spacer part and of the main chain in a different way. It has been found that an increase in the number of gauche bonds resulting from kink motions reduces the order parameter by a factor of 2 [2].

Results and discussion

The dynamics of the director reorientation in the nematic phase after a mechanical flip of about 90° can be characterized by the time dependence (Fig. 2) of the ^{1}H NMR line width, which runs through a minimum as is expected for nematic uniaxial systems.

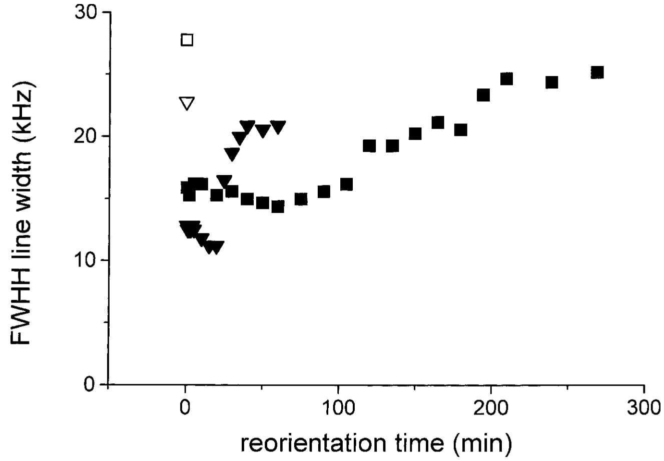


Fig. 2 The time dependence of the ^{1}H NMR line width after a sample flip [degree of polymerization of 26 (▼) and 154 (■)]. The *open symbols* denote the line width of the spectra in the equilibrium orientation before the mechanical flip has been carried out (*FWHH*: full width at half height)

We found that the reorientation behaviour was homogeneous for initial angles between the static field and the mean director of close to 90°; this has also been reported by several authors for the case of liquid-crystalline side-chain polymers [18, 19]. The accuracy of the 90° flip was about ±2°. For the data treatment the initial angle, α, in Eq. (2) was used as an adjustable parameter. Within the accuracy of the method, the time constant, τ_η, was independent of the initial angle. This behaviour is qualitatively different from the behaviour found for main-chain and lyotropic liquid-crystalline polymers, where back-flow effects can be observed for initial angles larger than 45°, resulting in a reduced effective viscosity [10]. However, in order to address the problem of inhomogeneity effects during the reorientation, a clear effect on τ_η would be necessary, which is not the case.

The molar mass dependence of the rotational viscosities of the samples is shown in Fig. 3 ($\gamma_1 \propto z^\beta$ with $\beta \sim 1.2$). The results are summarized in Table 2.

If the magnetic anisotropy parameters are known, the viscosites can be calculated or vice versa. Therefore, the value of the anisotropy of the magnetic susceptibility of a similar substance [9] ($\Delta\chi \sim 1.4 \times 10^{-6}$) was used. The anisotropy is positive, which results in alignment of the director parallel to the orienting field. It has been assumed that the magnetic anisotropy of the material does not depend on the degree of polymerization.

As discussed later, the dynamics can be used to estimate the order parameter in the nematic phase. Figure 4 gives typical angular dependences of the line width in the frozen glass at 20 °C, from which S can be

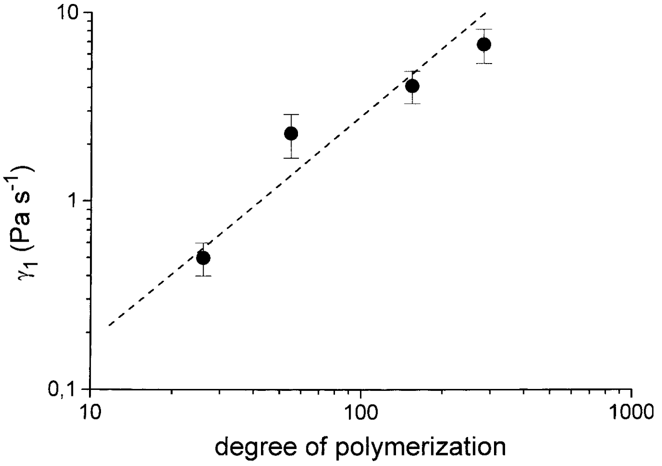


Fig. 3 The dependence of the rotational viscosities on z (from Table 2), which were obtained from the doublet splitting and τ_η according to Eqs. (2) and (3), the degree of polymerization (at $T_{N\text{–}I} - T \approx 15$ K). The *dashed line* corresponds to $\beta = 1.2$

Table 2 Rotational viscosities, γ_1, at $T_{N\text{–}I} - T \approx 15$ K measured at 60 MHz

Sample no.	Degree of polymerization, z	Orientation time τ_η (min)	Viscosity γ_1(Pa s)
P1-26	26	25	5 ± 1
P1-55	55	40	23 ± 5
P1-154	154	100	41 ± 8
P1-287	287	120	68 ± 10

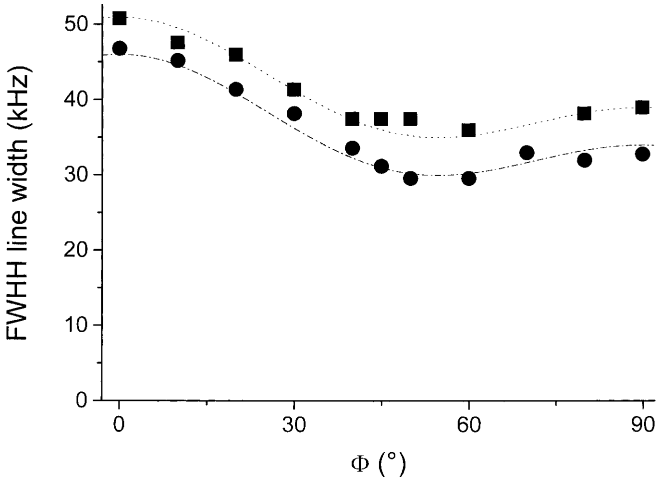


Fig. 4 Angular dependences of the ^{1}H NMR (at 60 MHz) line width of the frozen orientation in the glassy state at 20 °C [samples P1-26 (●) and P1-287 (■)]

estimated according to Eq. (5), assuming a value of 25.4 kHz (in case of $S = 1$) for the splitting of the dominating Pake doublet of the ortho protons (proton–proton distance of 0.241 nm) [9]. At 300 MHz, the narrow central peak of the proton wide-line spectrum becomes asymmetric (Fig. 5) with respect to the centre of the doublet spectrum caused by the chemical shift difference between phenyl and aliphatic protons. The intensity of the narrow line changes with temperature, indicating that a larger number of the spacer protons are not oriented at higher temperatures.

The behaviour reflects qualitatively the molar mass dependence with respect to the magnitude of the order parameter as well as with respect to the broadness of the orientational distribution function. A slightly higher order parameter in the case of the lower molar mass compared to the high molar mass sample can be taken from the angular dependence in Fig. 4. A typical angular dependence of the proton spectra of the frozen orientation measured at 300 MHz is shown in Fig. 6; this shows the characteristic minimum near the magic angle. As expected, the order parameter does not depend on the magnetic field strength.

The temperature dependence of the line width,which should be proportional to the order parameter, measured at 300 MHz is shown in Fig. 5; this is attributed to the frozen orientation in the glassy state.

In principle, it is also possible to calculate the order parameter in the nematic phase using the data from the reorientation experiments; however, the director orientation (angle Φ relative to the magnetic field) must be calculated from the line width or doublet splitting. Of course, the number of accumulations is limited in order to avoid averaging during the reorientation.The separation of the doublets reflects the macroscopic alignment, which allows the additional determination of the order parameter by means of reorientation experiments. The doublet splitting can be taken to a good approximation as being proportional to the order parameter. Experimentally, the angle $\alpha - \phi(t)$ can be obtained from the doublet positions $\delta(t) = \delta_{\max} P_2[\cos(\alpha - \Phi(t))]$ and is recorded as a function of reorientation time, where $\delta_{\max}$ is the doublet splitting in the equilibrium orientation ($d \parallel \mathbf{B}_0$).

Using this approach the order parameter could be calculated for the sample with the highest molecular weight at 90 °C to be about 0.43. The result is that S obtained from the reorientational dynamics after a sample flip is identical to that obtained from the static experiments. The order parameter does not depend on the molecular weight or on the magnetic field to which the samples have been exposed . The order parameters of the side chain (Table 3), which can be estimated from the proton results, are typical for nematic side-chain polymers. They are referred to with respect to the order parameter in the glassy state.

However, it must be mentioned that the use of ^{1}H NMR is far from being ideal because of the superposition of relatively featureless broad lines which cannot

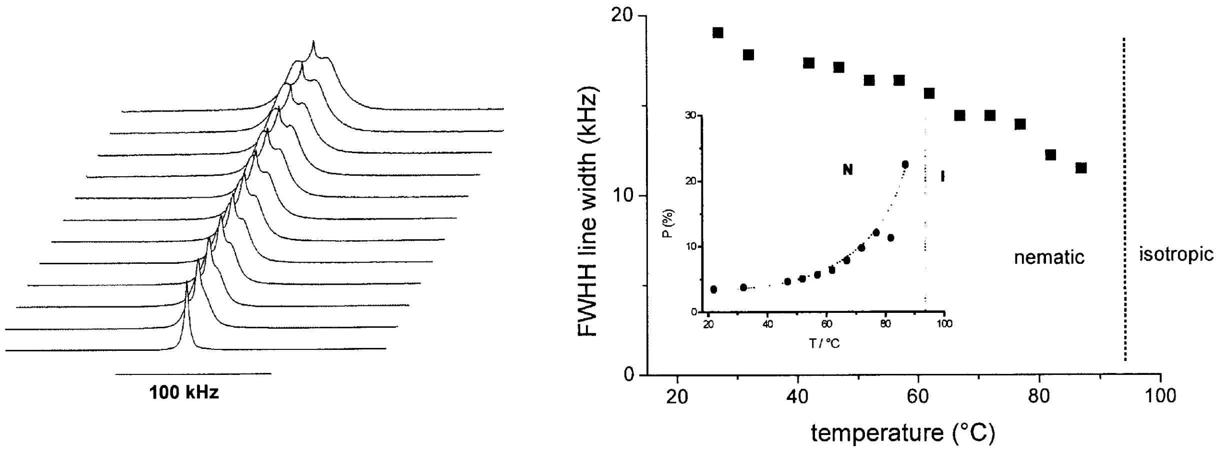


Fig. 5 Temperature dependence of the proton spectra (*left*) and line widths (*right*) of the low-molecular-weight sample P1-26 measured from higher to lower temperatures in order to avoid molecular reorientation. The temperatures (°C) are (from the *bottom*) 98, 87, 82, 77, 72, 67, 62, 57, 52, 47, 32, 22. The *insert* shows the amount of the population (%) of the narrow line contribution to the ^{1}H NMR spectrum

be decomposed. A site-specific resolution is not possible. The proton spectra (60 MHz) are a superposition of Pake doublets and central peaks with a residual line width of approximately 6 kHz for all molecular weights. This peak cannot be completely explained by freely rotating methyl groups (only 14% of the protons). In that case, the intensity must be independent of the molecular weight, which is not the case. However, the -O-CH_3 group inclines at an angle of about 55° relative to the para axis (or in oriented systems to the director orientation), which also provides, in addition to the mobility effect, a narrowing effect. Another explanation, supported by the line shape in the magic-angle passage during the reorientation process, is that part of the material is not oriented because of the unstructured narrow line at 55° (the line width seems to be identical to the central peak line shape in the orientation parallel to $\mathbf{B}_0$). Subtraction of the 55° spectrum provides a Pake pattern which could be observed for a side-chain polymer with a similar chemical structure [9]. Additionally, this central peak is fairly uninfluenced by the temperature, which also suggests two-component behaviour. Another explanation, and possibly in combination with the previous arguments, could be the drastically decreased orientation of the spacer in combination with some orientational distribution which also provides a residual line width in the "magic angle". However, it seems unlikely, that the spacer is completely unoriented and that the mesogenic group [12] carries the complete orientational order.

In contrast to the relatively high order parameter of about 0.66 (at 20 °C) in the side chain, the complementary set of ^{2}H NMR experiments at 46 MHz provides no (or no detectable) anisotropy in the angular dependence of the quadrupolar doublet splitting of methylene and methyl deuterons of the main chain, which might be expected according to Eq. (7), as shown in Fig. 7. The spectrum is a superposition of two powder spectra referring to the methylene and methyl deuterons. Despite the reduced signal intensity for the reorientation experiments in the nematic phase, the doublets could be

Fig. 6 The proton spectra (*left*) and the angular dependence of the line width (*right*) (sample P1-26) of the frozen orientation at 20 °C (at 300 MHz). The first spectrum is parallel to $\mathbf{B}_0$ and the last one is perpendicular to $\mathbf{B}_0$: Φ = 0°, 10°, 20°, 30°, 40°, 45°, 50°, 60°, 70°, 80°, 90°

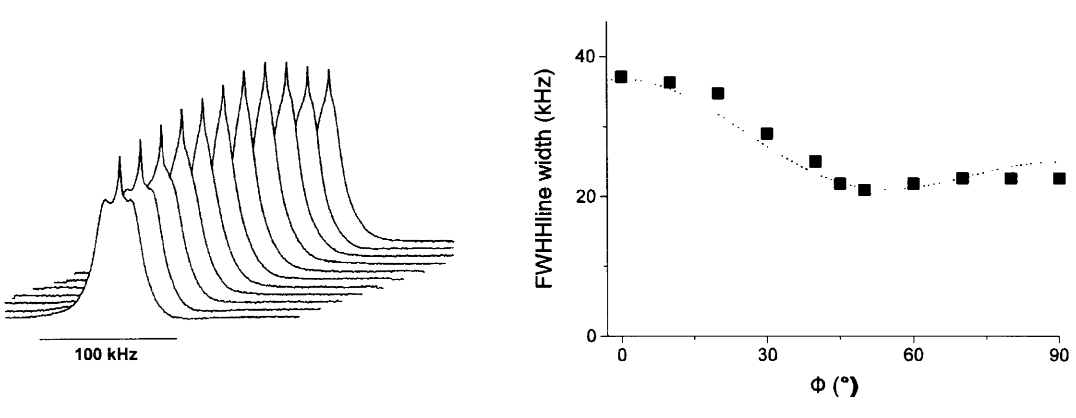


Table 3 Order parameters of the side chain

Sample no.	Degree of polymerization	Order parameter at 20 °C[a]	Order parameter at 90 °C from reorientation[b]	Order parameter at 90 °C and $\varphi = 0$ $\Delta\nu(90\ °C)/\Delta\nu(20\ °C)$
P1-26	26	0.66 ± 0.05		0.46 ± 0.05
P1-55	55	0.6 ± 0.1		
P1-154	154		0.43 ± 0.04	
P1-287	287	0.67 ± 0.05		0.46 ± 0.05

[a] Obtained from measurements at 300 MHz
[b] Obtained from measurements at 60 MHz

clearly resolved. However, no anisotropy during the reorientation process, which was measured simultaneously by means of ^{1}H NMR, could be detected.

The results obtained by NMR spectroscopy are in good correspondence with the results of the SANS method; however, it should be emphasized that SANS and NMR are sensitive to orientational effects on different length scales. SANS from deuterated samples of side-chain liquid-crystalline polymers was used to determine the dimensions of the backbone both parallel and perpendicular to the director (Table 1) [15, 16]. Polymer P1 tends to form (for degrees of polymerization greater than 26) an oblate conformation; however, the anisotropy of the polymer coil is rather insignificant. For example, for polymer P1-287 the anisotropy is only 1.12 ± 0.05. It was found [13] that within the experimental error of the method (SANS) the molecular weight practically does not influence the chain dimensions in the nematic phase (Table 1). Apparently, due to the small anisotropy of the main chain, the NMR method fails to determine its orientation. ^{2}H NMR spectroscopy is not responsive enough for a definition of the anisotropy of the main chain in the nematic phase in the polymers investigated. As shown in other work [2] good results by means of NMR could be obtained only for a smectic phase with a magnitude of anisotropy of a polymer coil of 3–4.

At higher temperatures, the deuterium resonance line shape is more complicated and has some additional features (Fig. 8).

The detailed discussion of these effects is not the purpose of this work. There was no hint at any exchange in a 2D-exchange experiment (mixing time of 5 ms) at 90 °C.

The weak proton–deuteron coupling on the main-chain–side-chain branching site complicates the attempt to pronounce the methylene deuterons in the spectra by means of ^{1}H-^{2}H cross polarization [20]. As mentioned previously, no anisotropy could be detected.

Conclusions

^{1}H and ^{2}H NMR investigations have been carried out in order to investigate separately properties of the main and side chain of a liquid-crystalline side-chain polymer with varying molecular weight. The side chain can be oriented in magnetic fields due to the anisotropy of the magnetic susceptibility in its nematic phase. The orientation can be frozen at temperatures below the glass-transition temperature. The orientational effect of the side chain is completely decoupled from the main chain, which shows no or only a very weak orientational order. The orientational dynamics of the side chains depends strongly on the molecular weight. The viscosity properties can be discussed using the common models of the

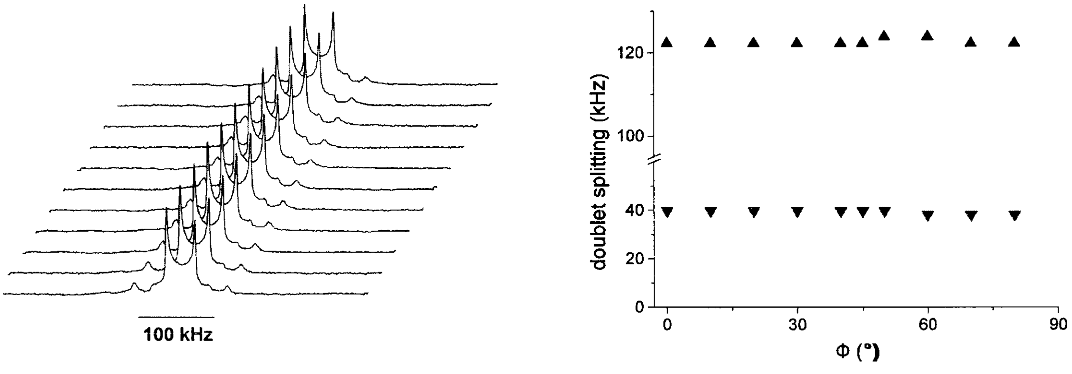


Fig. 7 The angular dependence of the spectra (*left*) and of the doublet splitting of the deuterium spectra (*right*) at 20 °C of the low-molecular-weight sample with a degree of polymerization of 26. The orientation achieved in the nematic phase is frozen (see ^{1}H NMR spectra). The lowest spectrum is parallel to $\mathbf{B}_0$ and the highest spectrum is perpendicular to $\mathbf{B}_0$: Φ = 0°, 10°, 20°, 30°, 40°, 45°, 50°, 60°, 70°, 80°, 90°; methylene deuterons (▼); methyl deuterons (▲)

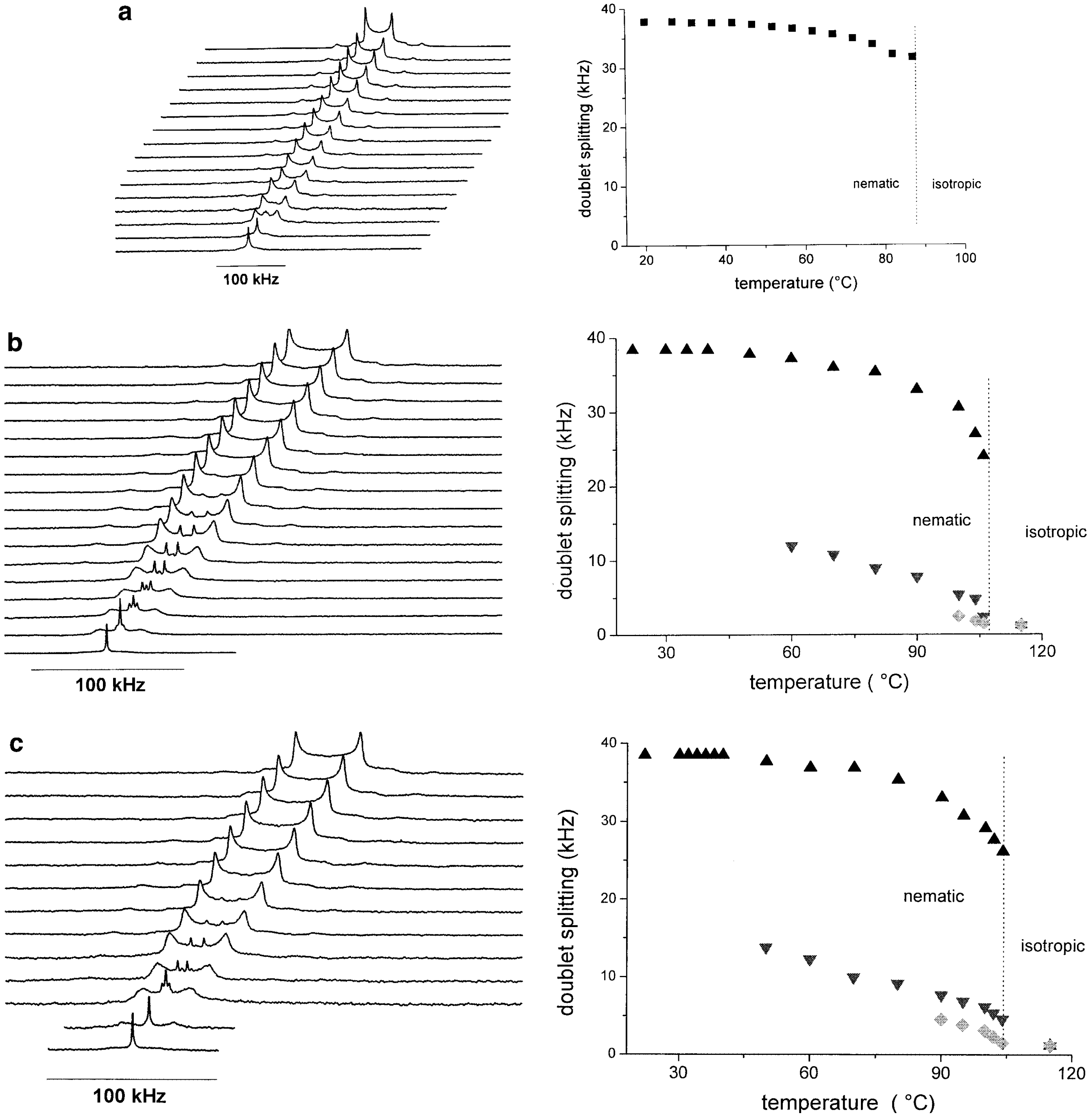


Fig. 8a–c The temperature dependence of the deuterium spectra (*left*) and the splitting of the doublets (*right*) of the quadrupolar spectra measured from higher to lower temperatures (samples P1-26, P1-154 and P1-287). The temperatures (°C) from the bottom are **a** P1-26: 103, 98, 87, 82, 77, 72, 67, 62, 57, 52, 47, 42, 37, 32, 27, 20; **b** P1-154: 115, 104, 102, 100, 95, 90, 80, 70, 60, 50, 40, 38, 36, 34, 32, 27, 20; **c** P1-287: 115, 106, 104, 100, 90, 80, 70, 60, 50, 40, 35, 30, 20

molecular-weight dependence; however, the proton spectra indicate a more complicated orientational behaviour and/or the coexistence of oriented and unoriented regions within the material. Further investigations are needed in order to address this problem, involving methods with higher resolution than ^{1}H NMR. The information obtained by NMR spectroscopy is in good accordance with the results of the SANS method.

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