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NMR Investigation of the Main-Chain Orientation in Liquid-Crystalline Side-Chain Polymers

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Summary: The main-chain orientation in different groups of liquid-crystalline side-chain polymers was investigated using several NMR techniques. For two polyesters the average orientation of the main chain in dependence on the main-chain spacer length could be found from 2D PASS experiments. In polysiloxanes with different mesogenic side groups and different spacer lengths this information could be received from chemical shift anisotropy measurements. Additionally, application of a modified β-echo allowed the separation of the dipolar ^{29}Si-^{29}Si interaction and to characterize the transversal anisotropy of the main-chain segments. Comparison with small angle neutron scattering results gave good agreement, where the different length scale of both methods has to be taken into account.

Keywords: liquid-crystalline side-chain polymers; main-chain orientation; polyesters; polysiloxanes; solid-state NMR

Introduction

The phase behaviour of liquid-crystalline side-chain polymers (SCLCP) is mainly influenced by the mesogenic character of the side chains. However also the structure of the *main chains* influences essentially some macroscopic features, like glass transition, viscous as well as elastic properties and sometimes also the phase behaviour. Thus the characterization of the main chains is necessary for establishing structure-property correlations and affects the development of new materials with better functional properties.

If the side chains form liquid-crystalline phases, the main chains are forced to accept also a certain degree of order. The mesogenes tend to built ordered phases, in this way they are minimizing the inner energy and because of that the free energy. The polymer main chains show a contrary behaviour and tend to develop random coils. This maximizing of the entropy corresponds to a lowering of the free energy, too.

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In investigations using small angle neutron scattering techniques [1] mixtures of deuterated and non-deuterated molecules were macroscopically oriented. They give information about the anisotrpy of the average molecular shape, characterized by the gyration radii $R_{||}$ and $R_{\perp}$ parallel and perpendicular to the side-chain director, respectively. From this investigations a rule was established, that SCLCP with a low-temperature smectic phase have also in the nematic phase molecules with oblate shape, whereas a prolate shape is observed from purely nematic SCLCP.

For NMR investigations of the main-chain orientation anisotropic spin interactions have to be used. One of them is the quadrupolar interaction observed in deuteron resonance. The advantage of these methods is a large information content from simple experiments [2], the drawback, that sample deuteration is needed.

The simplest way was, to try which information can be gained using the proton dipol-dipol interaction, because for the strong NMR signal only a few scans are necessary. However the unresolved multi-spin interaction gave almost structure-less lines and additionally there were some troubles with the data evaluations.

Another possibility is the use of the anisotropy of the chemical shift (CS) in ^{13}C NMR. Because of the larger number of resonances often multi-dimensional experiments are needed. High selectivity is achieved at the expense of larger experiment times. For such an application an example will be given in this paper.

The same interaction can also be used for siloxanes SCLCP's applying ^{29}Si NMR. Like for the NMR methods mentioned above, the determination of molecular orientation distribution needs information about the chemical shift tensor orientation within the molecules. In multidomain systems, axialsymmetry of the sample (uniaxiality) can be assumed. In much cases similarly transverse isotropy (symmetry with respect to a rotation around segment long axis) is taken into account. The latter, however, cannot be supposed a priori in SCLCP's. That means, another anisotropic interaction must be additionally included with a symmetry axis not being parallel to the chemical-shift symmetry axis. It will be shown that the dipolar interaction of ^{29}Si-^{29}Si pairs can be applied for this task.

Theoretical Background

Orientation distribution

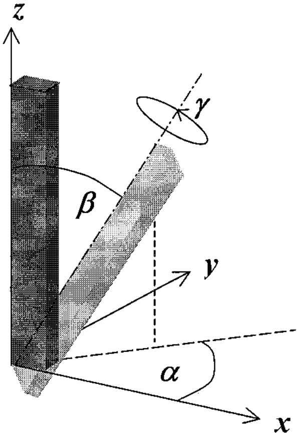

Figure 1. Characterization of the spatial orientation of an object by the Eulerian angles.

In an ensemble of differently oriented objects (e.g. molecules, segments of molecules) an individual orientation can be characterized by the Eulerian angles α,β,γ (see Fig. 1).

In a multidomain system the α dependence is expected to be uniform (axial symmetry), for the description of such an uniaxial sample we need a two-dimensional orientation distribution function (ODF) $V(\cos\beta,\gamma)$. If there is additionally no γ dependence, i.e. the system is transversely isotropic, then only the polar distribution $U(\cos\beta)$ is of interest.

As an alternative to the complete ODF, the coefficients from an expansion in basis functions are often used to characterize the orientation distribution. For the 1D case this is an expansion in Legendre polynomials (for 2D in spherical harmonics, for 3D in Wigner Rotation matrices [3]) in the following way:

$$U(\cos\beta) = \sum_{n=0}^{\infty}(2n+1)\langle P_n\rangle \cdot P_n(\cos\beta). \tag{1}$$

The orthogonality of the P_n permits the calculation of the expansion coefficients as

$$\langle P_n\rangle = \int_{-1}^{1} P_n(\cos\beta)U(\cos\beta)\,d(\cos\beta) = \begin{cases} 1/(2n+1) & \text{for complete orientation} \\ 0 & \text{for isotropic distribution} \end{cases} \tag{2}$$

$\langle P_n\rangle$ is denoted here as orientation degree of the n-th order.

If the orientation measurement uses the chemical-shift anisotropy, as an intermediate result the orientation degrees $\langle P_n\rangle_Q$ for the distribution of the chemical shift tensor symmetry axes with respect to the external magnetic field are obtained. To get the wanted distribution of the chain segments in relation to the director (corresponding orientation degrees $\langle P_n\rangle_S$), the direction of the tensor main axes must be known and the sample has to be oriented in the magnetic field, so that the director shows into the B_0 direction.

In the case of transversal isotropy the two kinds of orientation degrees are connected by (ε angle between the tensor symmetry axis and the segment direction)

$$\langle P_n \rangle_Q = \langle P_n \rangle_S \cdot P_n(\cos \varepsilon) \tag{3}$$

Transversal anisotropy

The problem of transversal anisotropy will be demonstrated in Fig. 2 by an simplified model of a polysiloxane side-chain polymer. Even though the three segments have nearly the same polar angle β, the different arrangement of the Si-O-Si plane in the main chain demands different rotations and conformations of the spacer and different excluded volumes. Therefore a non-equal distribution of γ must be expected.

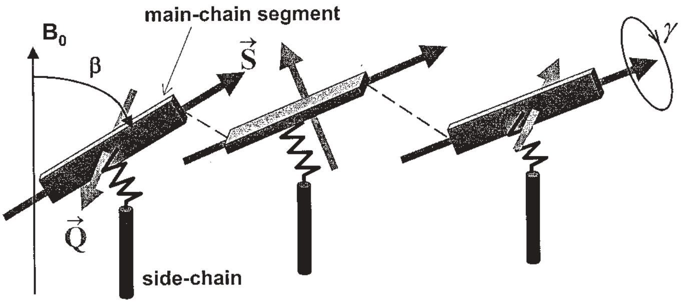

Figure 2. Model of the SCLCP polysiloxane. Q: CS-tensor symmetry axis; S: segment direction; zigzag: spacer; block: main chain segment (largest side: Si-O-Si plane).

For the case, that the CS-tensor symmetry axis is perpendicular to the segment direction, the following relation was derived using some simplifications [4]

$$\langle P_2 \rangle_Q = -\frac{1}{2} \langle P_2 \rangle_S + \frac{9}{32} \pi^2 \cdot q_2 \tag{4}$$

Here q_2 is the transversal-anisotropy parameter of second order (second Fourier coefficient of the transverse orientation distribution). The latter can be calculated, if the two orientation degrees can be measured separately, as will be shown later. Transverse anisotropy is characterized by vanishing q_2; then Eq. (4) corresponds to Eq. (3) with $\varepsilon = 0$.

Experimental

Samples

The two considered polyesters 6PBA*x* contain 4-(phenylazo)azobenzene as mesogenic units in the side chains which are coupled to the main chain by a spacer of 6 methylene groups. The number of methylene groups in the main-chain spacer is characterized by x (x = 8 or 13). The phase structures are (c 81 s_x 87 s_c 110 n 119 i) for 6PBA8 and (g 54 s_a 104 n 111 i) for 6PBA13. Synthesis and characterization of these substances are described in ref. [5].

Three different types of polysiloxanes were used named M*y*, D*y*, T*y* with two (M), three (D), and four (T) phenyl rings per side chain, coupled to the main chain by a spacer containing y methylene groups. The glass transition temperatures are between -5^0C and 30^0C. The majority of the samples do not have a low-temperature smectic phase; only M3, M5, and M6 show a smectic-A phase.

The samples were oriented in a magnetic field of 9.4 T in the nematic state. From 15 K below the nematic-isotropic point the temperature was set abruptly to the measuring temperature, at least 10 K below the DSC glass temperature. Because the latter process needs less than 1 min and the rotational viscosity of liquid-crystalline polymers is quite high at T_C – 15K, we can assume, that in this way there was no structural change during the quenching process.

NMR measurements

The NMR experiments were performed on a VARIAN INOVA-400 solid-state NMR spectrometer. Static proton-decoupled ^{13}C and ^{29}Si spectra were generated by cross-polarization magnetization transfer from the protons. This simple technique was sufficient in the case of ^{29}Si NMR because there is only one single resonance.

In the ^{13}C NMR experiments, because of the variety of chemically inequivalent carbons, Magic-Angle Spinning (MAS) in connection with a suitable multi-dimensional technique had to be applied to get sufficient spectral resolution and to regain the information about the chemical shift anisotropy from the side-band intensities, e.g. by a Herzfeld-Berger analysis [6]. After some attempts with a 2D rotor-synchronized MAS experiment proposed by Harbison et al. [7] and the so-called 2D- and 3D-ORDER techniques [8], the 2D PASS method [9] turned out to be the most efficient one for several reasons. This rotor synchronized 2D-MAS technique allows to observe the isotropic spectrum in the central trace of a 2D spectrum, whereas the next traces contain the side-bands of the order ±1, ±2, and so on. In this manner, one is able to obtain an orientation-sensitive side band spectrum for each isotropic position separately.

For the determination of the anisotropic dipolar interaction of ^{29}Si-^{29}Si pairs a quite other technique on the basis of the so-called β-echo [10] was necessary. This method consists in a suitable combination of several Hahn- and solid echoes and produces a signal of only those ^{29}Si which are coupled to another ^{29}Si; isolated spins do not contribute to this signal. With 4.7 % natural abundance, 9.4 % of all ^{29}Si are neighboured to another ^{29}Si in a long chain. Some modifications were introduced: The first $\pi/2$ pulse was substituted by (ramped) cross-polarization via the protons, and mainly, the Fourier transform of the echo evolution (denoted as β spectrum) yields a new tool for correlation of dipolar and chemical-shift interaction.

For recording spectra at different angles between sample director and the magnetic field, the sample was rotated by a stepper motor which was controlled by the spectrometer computer. These measurements were done at temperatures at least 10 K lower than the DSC glass transition temperature to avoid reorientation of the mesogenic side groups under the influence of the tilted magnetic field and to ensure that the thermal narrowing of the solid state NMR lines is negligible.

Results and discussion

Main-chain orientation in polyester liquid-crystalline side-chain polymers

In solids the electronic shielding depends on the spatial orientation of the electron cloud surrounding the nucleus. Therefore, as mentioned above, chemical-shielding anisotropy spectra can be used to investigate the molecular orientation in solids.

In the simplest case, already static ^{13}C NMR spectra give a qualitative information about the orientational behaviour, especially if one considers spectra recorded in dependence on the angle δ between sample director and B_0 (see Fig. 3; for definition of the angle δ see also Fig. 5).

For both samples, the δ dependence of the aromatic and ester positions shows the high order of the mesogenic side chains. The aliphatic resonances for the sample 6PBA13 show a shift by about 23 ppm between $\delta = 0^0$ and 90^0. With knowledge of the orientation of the methylene CS tensor it follows that in this sample the chain axes for an essential part of methylenes lie parallel to the sample director (for both kinds of spacers), whereas from the missing δ dependence of the shifts of the aliphatic resonances in 6PBA8 a quite different spacer structure can be concluded.

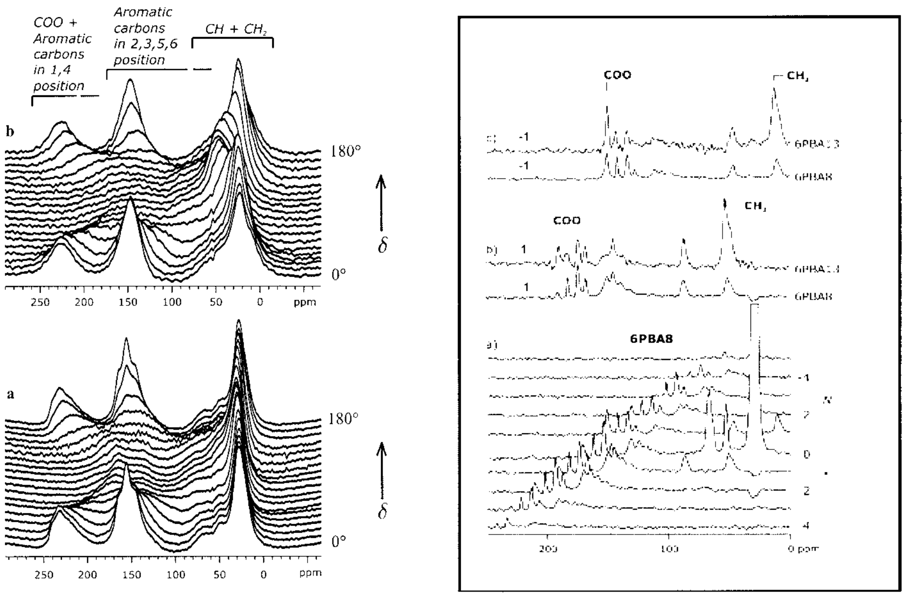

Figure 3. (left) Angle-dependent static ^{13}C spectra for the two polyester SCLCP. δ is the angle between the sample director and $\mathbf{B}_0$. (right) 2D PASS spectra: a) oriented 6PBA8, spinning side-bands of Nth order (N=0: central bands), b), c) Comparison of the spinning side-band traces for N = 1 and –1, respectively [11,12].

2D PASS spectra (Fig. 3) contain much more detailed information. The large differences between corresponding signals of the considered samples show ones more their different orientation.

Now the separated side-band intensities allow the determination of the orientation degree for the carboxyl group $\langle P_n\rangle_Q$ for $n = 2$ and 4. Defining the direction of the segment vector **S** as parallel to the line connecting the two ester carbons (e.g.in Fig. 4 (left) in the upper case **S** lies horizontally), and taking into account that the CS tensor symmetry axis shows in the direction of the CH-CO bond, the angle ε between those two directions is for tetrahedral symmetry of the four bonds of the methine carbon 90^0 minus the Magic Angle, i.e. $P_2(\cos\varepsilon) = 0.5$. According to Eq. (3), under the assumption of transversal isotropy, the segment orientation degrees $\langle P_2\rangle_S$ were calculated giving the values –0.46 and +0.28 for 6PBA8 and 6PBA13, respectively. With the mean angle $\langle\vartheta\rangle$ of the deviation from the director, defined by

$$\langle P_2\rangle_S = \frac{1}{2}\left(3\cos^2\langle\vartheta\rangle - 1\right) \qquad (5)$$

the possible main-chain direction inside a cone are visualized in Fig. 4 (left) and the preferred arrangement of main- and side-chains in Fig. 4 (right).

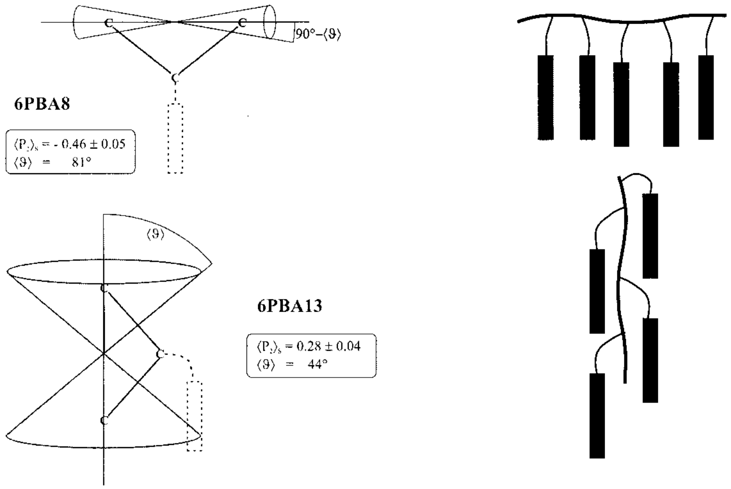

Figure 4. (left) Visualization of the main-chain order as revealed by the values of $\langle P_2\rangle_S$. The opening angles of the cones correspond to the mean angle of the deviation from the director $\langle\vartheta\rangle$. (right) Preferred mutual arrangement of side chains and main chains.

Main-chain orientation in polysiloxane liquid-crystalline side-chain polymers

Proton-decoupled ^{29}Si spectra recorded for incremented δ are shown in Fig. 5. The resulting orientation degrees of second order $\langle P_2\rangle_Q$ concerning the chemical shift tensor symmetry axis must again be recalculated to that ones according to the segment axis, at the moment again under the assumption of transversal symmetry. The segment direction is given by the connection of two neighboured Si atoms, but the orientation of the tensor symmetry axis was unknown. We got same experimental evidence, that this axis lies parallel to the interconnection of the two nearest carbons at an silicon, i.e. the angle ε is here 90^0, P_2 $(\cos \varepsilon) = - 0.5$. This tensor orientation was confirmed by quantum mechanical calculations [13] for the middle silicon of octamethyltrisoloxane.

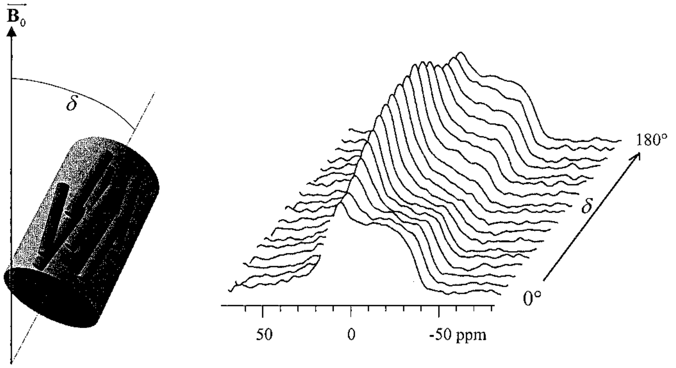

Figure 5. (left) Definition of δ as the angle between director of the mesogenic groups (rods) with respect to the external magnetic field $\mathbf{B_0}$. (right) δ-dependent static-sample ^{29}Si spectra of sample D11 [4].

The results are schematically presented in Fig. 6. It can be summarized, that in the most cases the main chains are arranged preferably perpendicular to the side chains. Within the M samples, only for M4 (contrary to M3, M5, M6) a parallel structure was observed. Finally, in some cases were perpendicular conformation would lead to sterical hindrances (cf. T3 in Fig. 5), also a parallel structure is preferred.

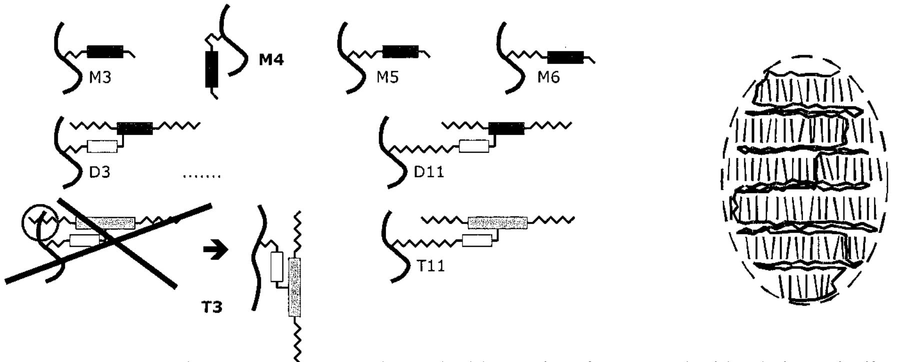

Figure 6. (left) Relations between main and side chains for several side-chain polysiloxanes.(explanation see text). (right) Possible molecular structure with prolate shape, but preferably perpendicular arrangement of the main chains to the side-chain director.

The parallel arrangement for M4 can be regarded in connection to the prolate shape of the whole molecule observed by SANS[1] which might be a reasonable correlation. If we conclude in an analogous manner that T3 will have a prolate shape and all others an oblate one we would arrive at an apparent contradiction to the rule established from SANS investigations [1] (see above) because no one of the D and T polysiloxanes exhibit a smectic phase at lower temperatures. Here it must be emphasized, that the SANS and NMR experiments were dealing with different length scales (whole polymer molecule or a single monomeric unit, respectively). On the right-hand side in Fig. 6 it is shown schematically that structures with prolate shape, but preferably perpendicular arrangement of main chains to side-chains are possible; this should be taken into account for comparing NMR and SANS data from SCLCP .[4]

Coupling of main chains and side chains

For the estimation of the main-chain reorientation speed in the nematic phase after a sudden orientation jump to an angle δ of 85^0 between director and magnetic field, ^{29}Si spectra were recorded at different times after the jump (Fig. 7).

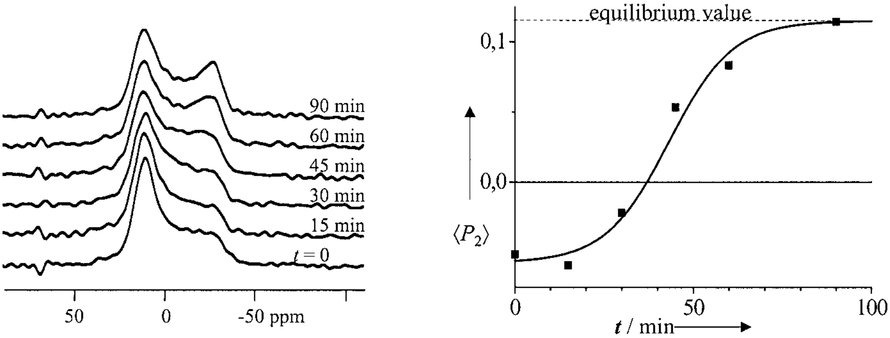

Figure 7. (left) Time-dependent static ^{29}Si spectra of sample M6 (nematic phase), which was rotated at t = 0 by 85^0 relatively to $\mathbf{B}_0$. (right) The $\langle P_2\rangle$ values calculated from the spectra at the left-hand side characterize quantitatively the evolution of the main chain. The solid line is the best fit to Eqn. (6).

From that the time dependence of the orientation degree was determined (Fig. 7). If the director field can be assumed as remaining homogeneously during the reorientation process the angle α between current director and external field evolves as

$$\tan\alpha(t) = \tan\alpha_0 \cdot \exp\left(-\frac{t}{\tau}\right) \tag{6}$$

A fit of the experimental data to $(3/2)\cos^2\alpha(t)-1/2$ yields the main-chain reorientation time τ = (17 ± 1) min. In an analogues proton experiment at the same temperature the reorientation time for the side chain was measured as (16.3 ± 0.1) min [14] which is equal to the main-chain value within the error limits.

This result demonstrates that static as well as temporary orientations of side and main chains are strongly correlated in spite of the highly flexible alkyl spacer. Although the individual side chains have a quite high mobility (proton $T_{1\rho}$ experiments yield overhead jump rates in the order of 10^5 s^{-1}), the whole side chain director is not able to reorient faster than the main chain. The magnetic torque on the director results in a deforming force on the main chain. The latter takes the new conformation only very slowly because of the large viscosity of the macromolecule. Only together with the main chains the side-chain director is able to rotate into a new direction. This mutual dependence corresponds to the concept of strong molecular-field coupling of both components.

Transversal anisotropy of the main chain

As mentioned above, transversal isotropy cannot be assumed a priori for the main-chain segments in SCLCP's; their complete orientation distribution must be represented by an at least two-dimensional function. Because of the axialsymmetry of the ^{29}Si CS tensor, orientations can be estimated by that as only one-dimensional polar-angle distributions of the CS tensor axes. Therefore, extraction of the full information demands the use of an additionally another anisotropic spin interaction with a symmetry axis not parallel to that of the CS-tensor. Principally the dipolar ^{29}Si-^{29}Si interaction can be used for a direct determination of $\langle P_2 \rangle_S$ of the main chains [15].

However, there are some problems to measure the dipolar ^{29}Si-^{29}Si coupling: (i) ^{29}Si has a low absolute NMR sensitivity: $3.7\text{x}10^{-4}$ compared with protons; (ii) ^{29}Si signals are mainly caused by isolated ^{29}Si nuclei, rather than about 10 % by ^{29}Si-^{29}Si pairs. (iii) The anisotropy of the chemical shift is one order of magnitude larger than the dipolar interaction, i.e. the resonance of spin pairs is nearly identical with that one of isolated spins. That means, even if one could separate the spectrum of the coupled spins, a determination of the coupling constants and by that way of the atomic distances would be impossible.

As described in the chapter 'NMR measurements', these difficulties could be circumvented by use of the β-echo technique. Here the signals from all those spins are eliminated which are not underlying a bilinear interaction. The relatively small dipolar spin-pair interactions can be monitored by the time dependence of the β echo which for a unique coupling constant ω is given by

$$\beta(\tau)=\frac{2}{3}\sin^2(\omega\tau) \tag{7}$$

(τ is the time between excitation and echo pulse), whereas a powder average over dipolar couplings gives the relation

$$\beta(\tau)=\exp(-\tau/T_2)\left\{1-\sqrt{\frac{\pi}{9\omega_D\tau}}\left[\cos\left(\frac{3\omega_D\tau}{2}\right)\cdot \mathrm{C}\left(\sqrt{\frac{9\omega_D\tau}{2}}\right)-\sin\left(\frac{3\omega_D\tau}{2}\right)\cdot \mathrm{S}\left(\sqrt{\frac{9\omega_D\tau}{2}}\right)\right]\right\}. \tag{8}$$

Here C and S are Fresnel integrals and the dipolar coupling constant ω_D is

$$\omega_D=\frac{3}{2}\frac{\gamma^2\hbar}{r^3}. \tag{9}$$

Fig. 8 shows the theoretical time dependence of the β echo for several dipolar coupling constants and compares a measured β echo curve for the sample M4 with a fit curve.

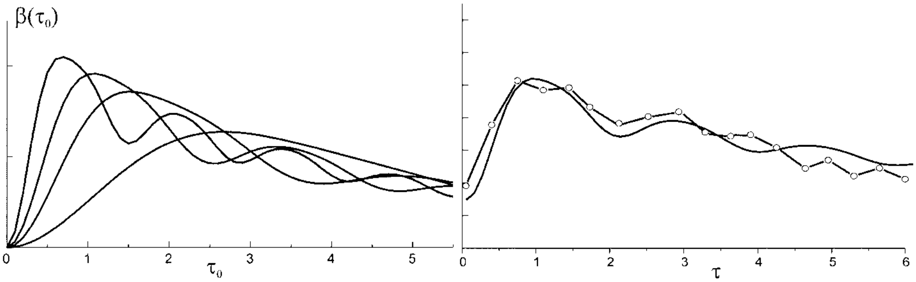

Figure 8. (left) Theoretical time dependence of the β echo for dipolar coupling constants ω_D/kHz = 0.1, 0.3, 0.4, 0.5, respectively, from right to left near the origin according to Eq. (8). (right) Comparison of the for M4 measured β echo (circles: measuring points) and a theoretical fit curve. Fit parameters see text.

From the latter we obtained the value of the dipolar coupling constant $\nu_D = \omega_D / 2\pi = (240 \pm 25)$ Hz, giving a distance between two neighboured silicons (3.1 ± 0.1) Å. With the known Si-O bond distance of 1.62 Å the Si-O-Si bond angle can be calculated as 145.6° ± 5°, as it were a by-product of the measurements.

To perform a selective analysis of the spectral components time evolution the β echoes were Fourier transformed (Fig. 9) to enable following the time development for each chemical shift value in horizontal direction. Fig. 9 shows a measured **β** spectrum for the sample M4 compared with the normal spectrum immediately after cross polarization.

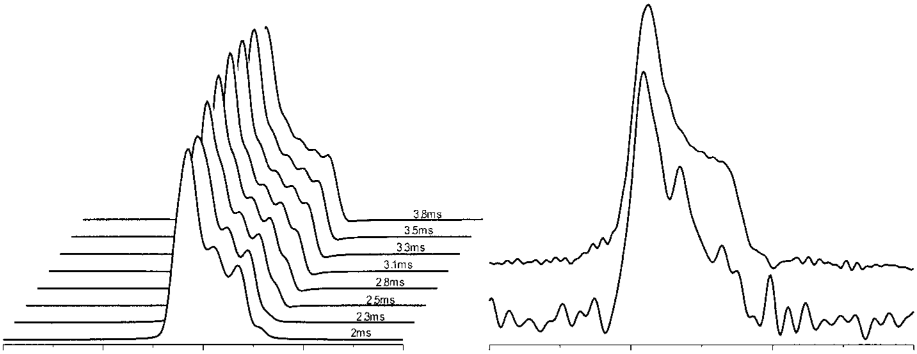

Figure 9. (left) Calculated time development of the β spectrum. (right) Experimental β spectrum (bottom) compared with the normal spectrum after a π/2 pulse (top), both for sample M4.

Tab. 1 shows the orientation degrees concerning segment direction $\langle P_2 \rangle_S$ and CS tensor symmetry axis $\langle P_2 \rangle_Q$ and the corresponding mean angles $\langle \vartheta \rangle_S$ and $\langle \vartheta \rangle_Q$ of the deviation from the director according to Eq. (5), and the transversal anisotropy parameter q_2, calculated according to Eq. (4), for the samples M4 and M6.

Table 1. Orientation degrees and mean angles of the deviation from the director concerning segment direction and CS tensor symmetry axis, transversal anisotropy parameter and mean angle concerning the transversal anisotropy, for M4 and M6 (see text).

	$\langle P_2 \rangle_S$	$\langle P_2 \rangle_Q$	$\langle \vartheta \rangle_S$	$\langle \vartheta \rangle_Q$	q_2	$\langle \gamma \rangle$
M4	$+0.27 \pm 0.02$	-0.092 ± 0.005	44^0	59^0	$+0.015 \pm 0.002$	42^0
M6	-0.31 ± 0.02	$+0.115 \pm 0.005$	69^0	50^0	-0.014 ± 0.002	47^0

The corresponding schematic results are demonstrated in Fig. 10. The values of q_2 show opposite signs compared with the value $q_2 = 0$ for transversal isotropy, leading to different angles of the segment 'blocks' around their length axis. In reality there is, of course, a distribution of this angle γ. However, if one uses for a better imagination the mean angles $\langle \vartheta \rangle_S$ and $\langle \vartheta \rangle_Q$ of the deviation from the director, the mean absolute value $\langle \gamma \rangle$ of the angle for the rotation around the segment axis for a known angle ε between segment- and tensor symmetry-axis is given by

$$\cos\langle\gamma\rangle = \frac{\cos\langle\vartheta\rangle_Q - \cos\varepsilon\cdot\cos\langle\vartheta\rangle_S}{\sin\varepsilon\cdot\sin\langle\vartheta\rangle_S}\,. \tag{10}$$

$\langle\gamma\rangle = 0$ means, the director, **S** and **Q** are aligned in one plane, i.e. the Si-O-Si plane is perpendicular to the drawing plane.

The values for $\langle\gamma\rangle$ in the case $\varepsilon = 90^0$ are listed in Tab. 1, too.

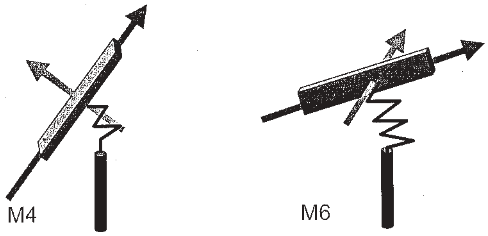

Figure 10. Resulting main-chain structure regarding the transversal anisotropy. Symbols see Fig. 2, explanation see text.

Conclusion

The main-chain orientation at the length scale of monomers could be estimated for a series of liquid-crystalline side-chain polymers. For polyesters ^{13}C NMR with MAS technique and multidimensional methods, especially the 2D PASS technique, have been used, whereas for silicon-containing polymers ^{29}Si resonance was applied. In both cases the anisotropy of the chemical shift was used.

The results show that NMR proves to be an alternative to scattering methods for the investigation of the orientation, particularly in systems with large disorder e.g. nematic or amorphous systems. However, in the comparison of the data interpretation from NMR measurements with that one of e.g. small-angle neutron scattering technique one has to take into account the different length scales, corresponding to a monomeric unit or to the whole molecule, respectively.

For the main-chain segments transversal isotropy could not assumed. In this case the transverse-anisotropy parameter q_2 represents an additional information about the structure. For the determination of that parameter, however, a second interaction with a symmetry axis not parallel to the CS-tensor symmetry axis must be applied. In the case discussed here, it was the dipolar interaction of ^{29}Si-^{29}Si pairs. But, because of some inherent difficulties, more complicated NMR experiments were necessary, to get a quantitative estimation of the transversal anisotropy.

The inclusion of the transversal anisotropy leads often to small quantitative corrections only. However, it can sometimes even result in a reversion of the sign of the orientation degree, leading to a miss-interpretation of the data, in extreme cases to a wrong calculation of the polar angle.

During the reorientation of a liquid-crystalline polymer in a switched external field, also the main chains have to be oriented into the new field direction. For some polysiloxanes the main-chain reorientation rate could be measured. It could be shown, that the reorientation of the mesogenic director is slowed down to that of the main-chain segments.

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