

Biaxial Nematic Phase in a Thermotropic Liquid-Crystalline Side-Chain Polymer

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We report on variable-angle deuterium NMR measurements of nematic liquid-crystalline side-chain polymers, where we have found proof of the existence of a biaxial nematic phase in a system with a side-on attachment of the mesogenic group to the polymer backbone. This provides efficient coupling to the polymer backbone and thus stabilizes the as yet elusive biaxial phase. The experimental approach is validated on a uniaxial end-on nematic polymer, and the reliability of the results is investigated in detail using two-dimensional correlation spectra, providing information on director distribution effects.

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Liquid crystals with biaxial nematic phases have been predicted theoretically by Freiser already more than 30 years ago [1]. His arguments, based on a generalized Meier-Saupe expression for the ordering potential of particles which deviate from axial symmetry, have stimulated a vast amount of theoretical and experimental work [2–7]. Importantly, it was shown that the Landau expansion of a mean-field free energy may be used to predict the existence of first-order isotropic (I) to biaxial (N_b) and second-order biaxial to uniaxial (N_u) phase transitions for particles with different shapes [2]. The sequence and order of the I- N_b - N_u phase transitions as well as the occurrence of a second-order I- N_b transition for particles exhibiting a particular axial ratio was confirmed by the solution of the mean field model [3], as well as by computer simulations [4].

Phase biaxiality is most straightforwardly proven by measurement of optical birefringence, commonly realized with a polarization microscope in the conoscopic mode, for which a macroscopically oriented sample must be aligned homeotropically with respect to its main ordering axis. However, problems associated with an unambiguous measurement, namely, the onset of transitions to crystalline or smectic phases as well as surface-induced ordering were already pointed out by Freiser [1]. Until now, there seems to be only one accepted experimental proof of a lyotropic N_b phase using nuclear magnetic resonance (NMR) [5]. Yu and Saupe successfully produced a macroscopically biaxial sample by repeated tilting and relaxation of the major director in a strong magnetic field and subsequently observed the NMR spectra of the deuterated water resonance at orientation angles 0° and 90° of the major director. The comparison of such spectra directly yields a biaxiality parameter (*vide infra*).

Yet, micellar aggregates in lyotropic systems such as the one investigated by Yu and Saupe are known to undergo vast shape changes with sample composition and temperature; it is not clear whether the shape of the aggregates is dynamic or whether such a system may even be a mixture of differently shaped aggregates [6].

Therefore, the discovery and investigation of a thermotropic biaxial nematic system of mesogens with fixed dimensions is of considerable interest. Luckhurst, Kothe, and co-workers [8,9] have published attempts to determine the potential biaxiality of low molecular weight thermotropic systems, such as alkyl-substituted cinnamic acid dimers [8] or a wedge-shaped derivative of biphenyl benzoate [9], for both of which birefringence data suggested biaxiality. Because of the low viscosity of such systems, deuterium NMR spectroscopy under continuous sample rotation [10] was applied by these authors. However, effects of biaxiality were never apparent within the error limits of their method.

We report on deuterium NMR experiments of a side-on [11] liquid crystalline side-chain polymer carrying a calamitic mesogen with enhanced lateral polarizability [12]. The side-on attachment of the mesogen to the polymer chain is successful in hindering the rotation about the molecular long axis and in preventing the formation of crystalline and smectic phases. We present data in support of earlier conoscopic observations, where phase biaxiality was claimed to be discovered in a binary mixture of such a side-on polymer and a low molar mass mesogen [13]. We have made measurements on a polymer with a similar mesogenic group as in earlier work, but with a siloxane backbone [14], which has the advantage of a substantially lower glass transition range (T_g), allowing investigations of undiluted bulk systems. We compare our results with a conventional siloxane-based end-on nematic polymer [14], which in addition exhibits a low-temperature smectic phase due to the absence of lateral substitution of the mesogen. The thermal properties of both samples are collected in Table I (chemical structures are shown in Fig. 2).

The samples were doped with 2% w/w hexamethylbenzene- d_{18} (HMB) as a quadrupolar spin probe, and ^2H NMR measurements were performed at $B_0 = 11.7$ T ($\nu_{L,^2\text{H}} = 76.8$ MHz). As in the work of Yu and Saupe [5], we derive the biaxiality of the samples from measurements of the quadrupole splitting, $\Delta\nu(\beta)$, at different angles β between the principal director of an

TABLE I. Thermal properties and activation parameters for director relaxation of the HMB-doped samples. Doping shifted the transition temperatures by 1 K on average.

	Side-on polymer	End-on polymer
T_g	279 K	275 K
Δc_p at T_g	0.9 J/g K	0.6 J/g K
T_{ni}	330 ± 2 K ^a	374 ± 2 K ^a
ΔH_{ni}	2.5 J/g	2.7 J/g
T_{sn}	...	317 K
ΔH_{sn}	...	~ 1 J/g
k_0 ^b	4×10^{29} s ⁻¹	5×10^{25} s ⁻¹
E_a^{app} ^b	190 kJ/mol	170 kJ/mol

^aIntervals indicate the width of the 2-phase region as determined by NMR.

^bMeasured at $B_0 = 11.7$ T.

annealed monodomain and the magnetic field,

$$\nu_q(\beta) = \nu_0 \pm \frac{3}{4}q_{zz}[\frac{1}{2}(3\cos^2\beta - 1) - \frac{1}{2}\eta\sin^2\beta], \quad (1)$$

where ν_0 is the ^2H resonance frequency, q_{zz} is the z principal component of the quadrupole interaction tensor in its principal axis frame, and η denotes the asymmetry (or biaxiality) parameter defined by

$$q_{xx,yy} = -\frac{1}{2}q_{zz}(1 \pm \eta). \quad (2)$$

The above relations are based on the rotation of boardlike mesogens (approximately prolate order tensor) around the q_{xx} direction.

The q_{ii} are proportional to the principal values of the susceptibility tensor, χ_{ii} , which in the case of rodlike aromatic mesogens orients with its least negative component $\chi_{zz} \parallel B_0$. These values are further proportional to the components of the generalized Saupe ordering matrix in

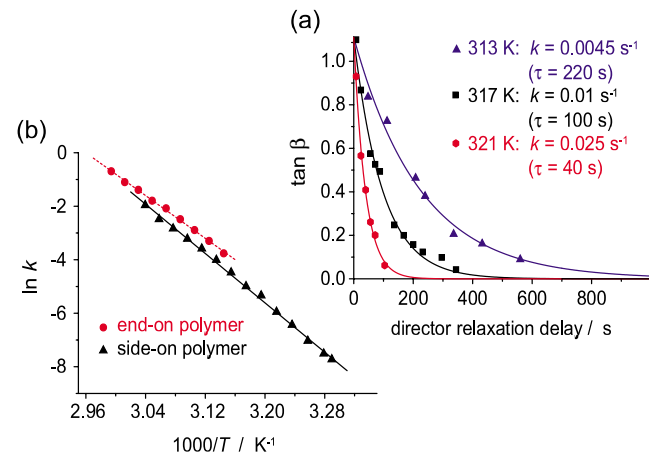


FIG. 1 (color online). Relaxation of the major director for the investigated polymers after a rapid sample flip to $\beta_0 = 48^\circ$. (a) Average director orientation for the side-on polymer as calculated from the spectral splitting for variable waiting times t after the flip, and fits to $\tan\beta(t) = \tan\beta_0 e^{-kt}$. (b) Arrhenius plot of the so-obtained rate constants, k .

its diagonal form, S_{ii} . The absolute values of the order parameters are not accessible due to the use of a spin probe as opposed to a mesogen-fixed deuterium label. In order to produce a macroscopically three-dimensional orientation of a potentially biaxial mesophase, the sample should in principle undergo repeated rotation and relaxation of the major director (q_{zz}), so as to force the secondary directors (q_{xx} , q_{yy}) into a minimal energy configuration [5]. Then q_{xx} , which is on average orthogonal to the aromatic plane of the mesogen (and is also associated with the most negative χ_{xx}) will point along the rotation axis.

The rotational viscosity associated with director relaxation can be expected to couple to the dynamics of the polymer chain and therefore to be sensitively influenced by the slowdown of chain modes when T_g is approached. We have therefore studied the director relaxation dynamics in the experimentally relevant temperature range (Fig. 1). Both activation parameters, the apparent activation energy as well as the frequency factor (see Table I), are found to be unrealistically large. These findings support the assumption of strong coupling, as the figures are typical for polymers, which usually exhibit a Williams-Landel-Ferry rather than an Arrhenius-type behavior [15]. The characteristic downturn of $\ln k$ upon approaching T_g is not apparent within the accessible temperature range. The upper limits are set by T_{ni} and the lower limits by excessive line broadening and T_{sn} for the side-on and the end-on polymers, respectively.

The relaxation times of the principal director in the investigated polymers range between around 0.4 and 2000 s. In particular at high T , the measurement of a

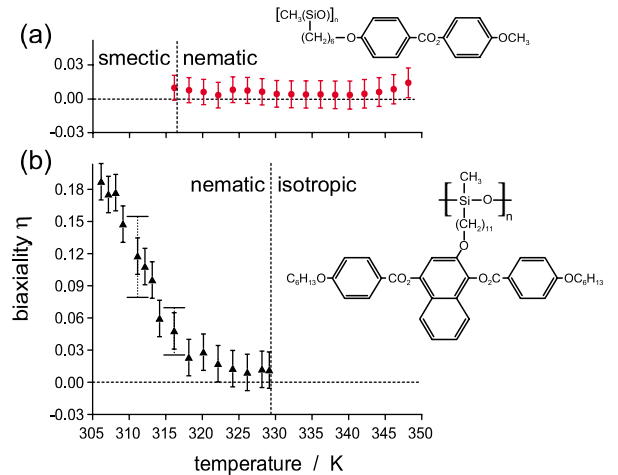


FIG. 2 (color online). Biaxiality parameters, η , for the end-on (a) and the side-on (b) polymers, as determined from the spectral splittings at $\beta = 0^\circ$ and 90° using Eq. (1): $\eta = 1 - [2|\Delta\nu_q(90^\circ)|/|\Delta\nu_q(0^\circ)|]$. Small error intervals are based on average reproducibility and reliability of line-shape fitting; the two larger error intervals in (b) were derived from two-dimensional experiments [see Fig. 3(b)]. Data for the smectic phase in (a) are not available due to phase separation of the spin probe.

sufficient number (several hundreds) of transients of a solid-echo quadrupole spectrum is not possible without considerable director relaxation on the experimental time scale. (Note that Yu and Saupe investigated a slowly relaxing lyotropic system and detected the signal of abundant D₂O, yielding a sufficient signal within only a few transients.) We have solved this problem by using a homebuilt probe head capable of rapid sample flips and synchronizing the flip with the pulse program [16], thus positioning the sample at the desired angle β only for the duration of the actual pulse sequence including acquisition (about 50 ms) and placing it back at the $q_{zz} \parallel B_0$ position during the comparably long recycle delay (1 s).

The sample flip including stabilization was measured to be complete within 150 ms. Fast director relaxation on this time scale would also challenge this approach and mimic phase biaxiality, due to a diminished spectral splitting for $\beta = 90^\circ$. The results obtained for the end-on polymer plotted in Fig. 2(a) indicate that a uniaxial nematic phase is reliably measurable even for director relaxation times much below 1 s. The weak tendency to increasing η at $T > 340$ K marks the onset of director relaxation during the stabilization delay. Inertial flow effects can be ruled out on the same basis, as well as by the observation of perfect matching of experimental $|\nu_q(\beta)|$ at different β and the theoretical prediction, Eq. (1).

The pronounced increase of the biaxiality parameter upon decreasing T for the side-on polymer plotted in Fig. 2(b) provides the first NMR proof of nematic phase biaxiality in a thermotropic system. The effect appears to be rather small when compared to the results of Yu and Saupe, who observed an η covering the full range between 0 and 1, accompanied by a sign change of the order parameter upon going from disklike to rodlike aggregates. Nevertheless, our result appears unambiguous within the error limits (*vide infra*). The isotropic to nematic phase transition at 330 K is observed to be weakly first order, with a typical value of $\Delta H = 2.5$ J/g. A decision whether this transition occurs directly into a biaxial state or whether a uniaxial phase becomes biaxial through a subsequent second-order transition at slightly lower T cannot be made on the basis of our data. A point worth mentioning is that we were not able to experimentally verify a planar polydomain of q_{xx} and q_{yy} , i.e., the tilting/relaxation procedure to produce a monodomain was not necessary. This sets an upper limit of some hundreds of ms for the relaxation time of the minor directors and confirms that orientation of $q_{yy} \parallel B_0$ rather than viscosity effects leads to monodomain formation.

We were most concerned with excluding potential systematic errors which could mimic our observation of biaxiality, as the spectra of the two polymer samples, especially those of the apparently biaxial side-on polymer, exhibit considerable spectral broadening. In particular for $\beta = 90^\circ$ do the two components of the doublet

overlap, challenging the determination of $\Delta\nu_q$ by simply reading off the maxima. Under the assumption of exponential relaxation, spectra were therefore fitted with two Lorentzians separated by $\Delta\nu_q$. Note that the central region of the spectra, where a narrow singlet attributed to isotropically mobile HMB in phase-separated siloxane or solvent impurities appeared, was excluded from the fits.

It is vital to experimentally prove the presence of a homogeneously broadened doublet. Otherwise, an underlying heterogeneous broadening, caused by a (quasi-)static distribution of director orientations, might interfere with a precise determination of η . First, we have conducted solid-echo experiments, so as to measure a T_2^* relaxation time independently of a potential distribution of ν_q . The values determined at $\beta = 0^\circ$ ranged from 1 ms down to about 0.3 ms between 330 and 311 K, and about half as much for $\beta = 90^\circ$. In this way, we could estimate that about 80% of the linewidth is due to homogeneous T_2^* effects, probably as a result of a coupling of the principal director fluctuations to slow dynamics of the polymer backbone. Accordingly, the linewidth increased considerably upon approaching T_g . First-order contributions to the broadening (e.g., susceptibility effects) were proven to be negligible using Hahn-echo measurements. Direct

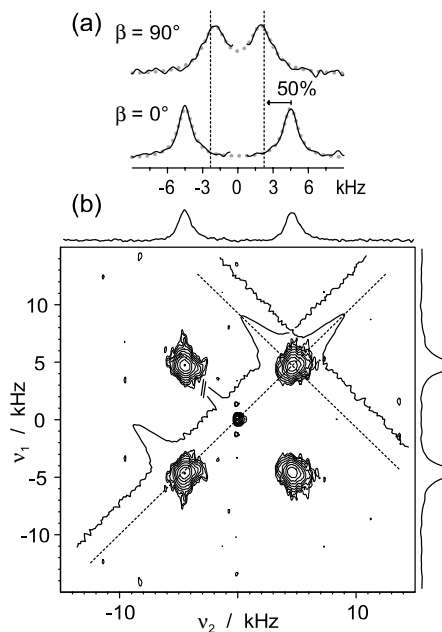


FIG. 3. Spectra of the side-on polymer acquired at 311 K. (a) One-dimensional spectra for different angles β and Lorentzian fits (dotted lines). (b) Two-dimensional ²H correlation spectrum (Hahn echo in the ν_1 dimension, followed by direct acquisition in ν_2 , cosine data set, 200 Hz line broadening in both dimensions) for $\beta = 0^\circ$, along with various projections. The quadrupolar splitting appears in both dimensions, as is apparent from the intensity contours in the 2D map. The comparison of linewidths of projections along the diagonal and the anti-diagonal (1360 and 1200 Hz FWHM, respectively) provides a basis for the estimation of the larger error intervals shown in Fig. 2(b).

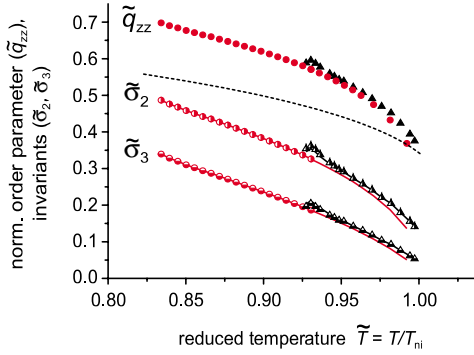


FIG. 4 (color online). Normalized z eigenvalue of the quadrupole tensor (order parameter) $\tilde{q}_{zz} = (q_{zz}/q_{zz,\text{ref}}) = [\Delta\nu_q(0^\circ)/16 \text{ kHz}]$ and tensor invariants for the side-on polymer (triangles) and the end-on polymer (circles), plotted as a function of reduced temperature. The invariants were calculated from the reduced \tilde{q}_{zz} . $\frac{3}{2}q_{zz,\text{ref}} = 16 \text{ kHz}$ represents an upper limit for the splitting observable under conditions of perfect coupling of the spin probe to the director field; the value corresponds to an HMB molecule jointly rotating around the phenyl ring normal and a second, orthogonal axis. Solid lines are calculated from \tilde{q}_{zz} assuming $\eta = 0$, and the dashed line is the (scaled) mean-field prediction of Meier and Saupe [18].

information on heterogeneous contributions to the line shape can be obtained by two-dimensional separation [17], as demonstrated in Fig. 3(b). Using the heterogeneous contribution to the linewidth for estimates of a potential error in η , it is seen in Fig. 2(b) that the reported biaxiality is robust within these rather conservative error intervals. Details concerning the static director distribution as well as investigations of the surprisingly fast relaxation of the minor directors will be reported elsewhere.

Finally, we turn to a test whether the Landau theory is able to provide a description of our data. In case of a biaxial nematic phase, the Landau free energy

$$G = a\sigma_2 + b\sigma_3 + \frac{1}{2}c\sigma_2^2 + d\sigma_2\sigma_3 + \frac{1}{2}e\sigma_3^2 \quad (3)$$

is expressed as a function of the fundamental invariants of the order tensor [1,7]:

$$\sigma_2 = \frac{2}{3}(q_{xx}^2 + q_{yy}^2 + q_{zz}^2) = \frac{2}{3}q_{zz}^2(\frac{3}{2} + \eta^2), \quad (4)$$

$$\sigma_3 = 4q_{xx}q_{yy}q_{zz} = q_{zz}^3(1 - \eta^2). \quad (5)$$

Note that $\sigma_3^2 \neq |\sigma_2^3|$ only when the phase is biaxial. In the biaxial state, $\sigma_3^2 \leq \sigma_2^3$ when the overall order parameter is positive (as is the case for calamitic mesogens). In the simplest mean-field approach, only the coefficients a and b are assumed to be linear functions of temperature. With the absolute minimum of G at [7]

$$\bar{\sigma}_2 = \frac{bd - ae}{ce - d^2} \quad \text{and} \quad \bar{\sigma}_3 = \frac{ad - bc}{ce - d^2}, \quad (6)$$

it follows that $\bar{\sigma}_2$ and $\bar{\sigma}_3$ realized in the biaxial phase should be linear in temperature. From Fig. 4, we infer deviations from this prediction, with $\bar{\sigma}_3$ being most nearly linear in T/T_{ni} . Further, the temperature dependence of the order parameter (q_{zz}) significantly exceeds the prediction of Meier and Saupe [18]. It must be emphasized that the finite η does not change the two invariants of the side-on polymer by more than 4% (solid lines), indicating that the thermodynamics of the system is dominated by q_{zz} . To which extent the weak biaxiality and the nature of the observed phase transition(s) are influenced by coupling to elastic and dynamic properties of the polymer [19] remains a subject of future experimental and theoretical work, for which we here hope to have provided a new, promising and fruitful perspective.

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