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De Vries smectic A phase formed by a liquid crystal side chain copolymer? A ^{13}C NMR study

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We study the orientation and order parameter of a liquid crystalline random side chain copolymer by ^{13}C NMR. Evidence has previously been presented that this material forms a de Vries smectic A phase. The NMR data show that the molecular tilt angle in the smectic A phase is very small or zero and the smectic A–smectic C* transition is attributed predominantly to a change of the molecular tilt rather than azimuthal ordering. We discuss the NMR results in the context of earlier X-ray and elastic characterizations of structurally similar materials.

1. Introduction

In recent years, liquid crystal elastomers (LCEs) have received considerable interest since they are rubbers with anisotropic optical, mechanical and electrical properties [1–6]. Because of this unique combination of properties, they open perspectives for novel non-display applications, e.g. in sensors or actuators. LC elastomers possess a number of interesting features, in particular when they are prepared as monodomain systems (single crystal liquid crystal elastomers, SCLCEs). The desired sample orientation can be obtained, for example, by mechanical stretching during preparation [7, 8] or by crosslinking of free-standing films [9]. LCEs are also interesting because of the interactions between mesogen orientations and macroscopic sample shapes. On a microscopic level, they are characterized by the orientational order of the mesogenic groups as well as an anisotropy of the elastomer network, and in smectic phases by an additional layer ordering of the mesogenic groups. The electrical and optical characteristics of LCE materials depend on the microscopic structure—order and orientation of the mesogenic molecular segments, and the smectic layering. The existence of piezoelectricity is one important effect in smectic elastomers formed from ferroelectric liquid crystalline polymers [9–13].

The structure and mesogenic properties of the precursor polymer essentially determine the mechanical, electrical and optical properties of the elastomer. Phase

transitions are only moderately influenced by crosslinking, the mesomorphism remaining essentially unchanged [10, 11]. This paper reports an investigation of a diluted random side chain siloxane copolymer which forms the basis for the synthesis and preparation of smectic elastomers studied in a variety of electric, mechanical and X-ray experiments [9, 12–15]. The chemical structure of the polymer is shown in figure 1. In order to avoid spontaneous, thermally induced crosslinking during the experiments, we chose a material that does not contain photoreactive groups, otherwise the compound is equivalent to the material used in earlier X-ray and mechanical measurements [12–18]. This detail should not affect the mesophase properties investigated here.

Homopolymers with the same structural elements as the diluted copolymer studied here, but with all the main chain segments substituted by mesogenic groups, have been found to form conventional smectic A (SmA) and smectic C* (SmC*) phases [17]. In a previous study, evidence was presented that diluted side chain copolymers (i.e. materials in which only a fraction of the main chain segments are substituted by mesogenic side groups) form a structurally different smectic A phase, a so called ‘de Vries’ type SmA structure [18]. For the material considered here and referred to as BR162A, the phase transition SmC* to SmA is second order and experimental evidence supporting the structural de Vries model [17, 18] has been derived mainly on the basis of X-ray data. The small angle X-ray scattering patterns show only very small thickness changes in the smectic layers at the SmA–SmC* phase transition, in contrast to

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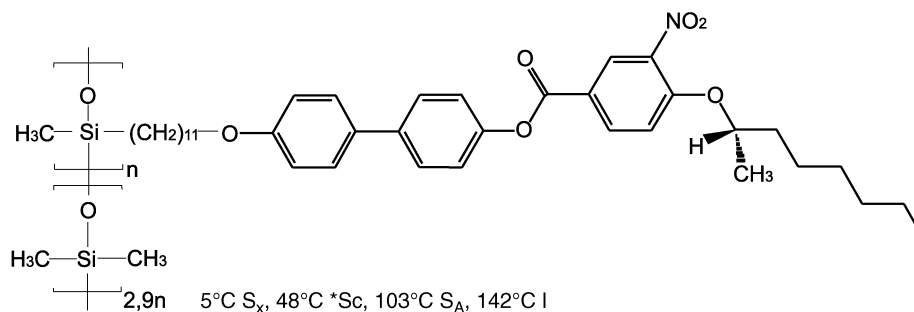


Figure 1. Chemical structure and mesophase sequence of the diluted random copolymer, BR162A.

the homopolymer with the same backbone and substituents. However, the X-ray and optical data presented, for example, in [14, 17, 18] can probe microscopic order parameter and molecular orientations only incompletely. We present here an NMR investigation of the polymeric precursor, in order to test the previous model and conclusions. Phase transitions, order parameter and orientations of mesogens and smectic layers with respect to the external magnetic field are studied by means of ^1H and ^{13}C nuclear magnetic resonance.

2. Experimental

The ^1H and ^{13}C NMR measurements were performed in a magnetic field of 11.7 T and corresponding resonance frequencies of 500.13 and 125.7 MHz for ^1H and ^{13}C nuclei, respectively, using a MSL500 spectrometer (Bruker Analytik GmbH). The samples (approx. 500 mg) were confined in standard 5 mm tubes, and measurements were performed in the temperature range 350–413 K. Temperature was controlled to ± 0.5 K; however, the strong rf power necessary for proton decoupling in the ^{13}C spectra of smectic phases heats the samples systematically to about 3 K above the controller settings. This can be checked, for example, at the phase transitions. ^{13}C NMR spectra in the isotropic state were recorded using $\pi/2$ pulse excitation together with WALTZ decoupling. In the liquid crystalline phases, proton decoupling was achieved by continuous high power irradiation or WALTZ cycles. With delay times between 4 and 5 s and >1000 accumulations for each FID, the time for the acquisition of ^{13}C spectra was at least 1.5 h. If not otherwise indicated, the samples were heated into the isotropic phase (temperature $\approx 142^\circ\text{C}$), before the temperature dependence of the NMR spectra was measured from high to low temperatures.

3. Results

^1H NMR is a competitive and quick method for the measurement of the orientational order, and we use it to determine the phase transition from the isotropic to the

SmA phase, see figure 2. In the isotropic phase, the individual lines of protons in the aromatic core and in the aliphatic chains are resolved by their different chemical shifts. The phase transition into the SmA phase is detected by the gradual broadening of the lines due to dipole–dipole interactions. The transition interval is approximately 5 K.

In the smectic phases, the proton NMR spectra consist of a non-structured broad line of approximately 20 kHz line width. This line shape (see figure 2, top) is not suitable for obtaining detailed information on the mesogenic orientation.

In order to explore conformations and ordering of the mesogenic units in the smectic phases, ^{13}C NMR measurements were carried out. Typical proton-decoupled ^{13}C NMR spectra in the isotropic and SmC phases for BR162A are shown in figure 3. Since the dipolar interactions with protons are broadband decoupled, the spectra are determined essentially by the chemical shifts of the individual carbon positions. An exception are carbons in the vicinity of nitrogen nuclei. Their lines are considerably broadened by ^{14}N – ^{13}C interactions, and they will not be accessible for evaluation of the spectra. The assignment of the carbon lines in the isotropic phase has been achieved using standard increment systems for the chemical shifts, and verified by comparison with spectra of structurally similar mesogens [19–22].

Due to the chemical shift anisotropy, the individual carbon lines change their resonance frequencies at the transition from the isotropic to the SmA phase, and they shift further within the smectic phases if the orientational order parameter or configuration of the polymer changes. Lines originating from the aromatic carbons have considerably larger anisotropies than those of the aliphatic chain carbons. Since these anisotropies contain the basic information about mesogenic order and orientation, we restrict our analysis to the aromatic part of the spectra where the effects are most pronounced and easier to observe. If the molecular conformation remains unchanged in all

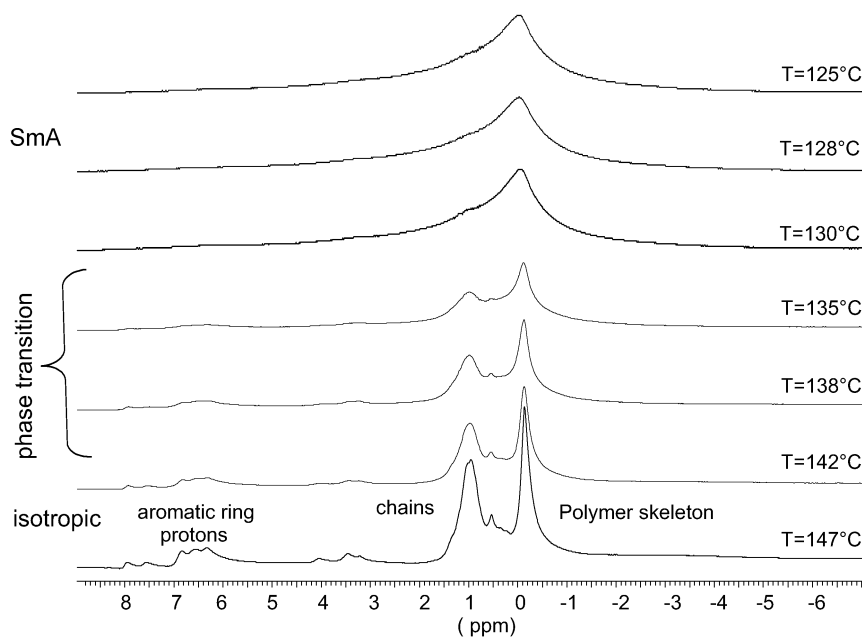


Figure 2. Temperature dependence of the proton-decoupled ^1H NMR spectra of BR162A at 500 MHz resonance frequency.

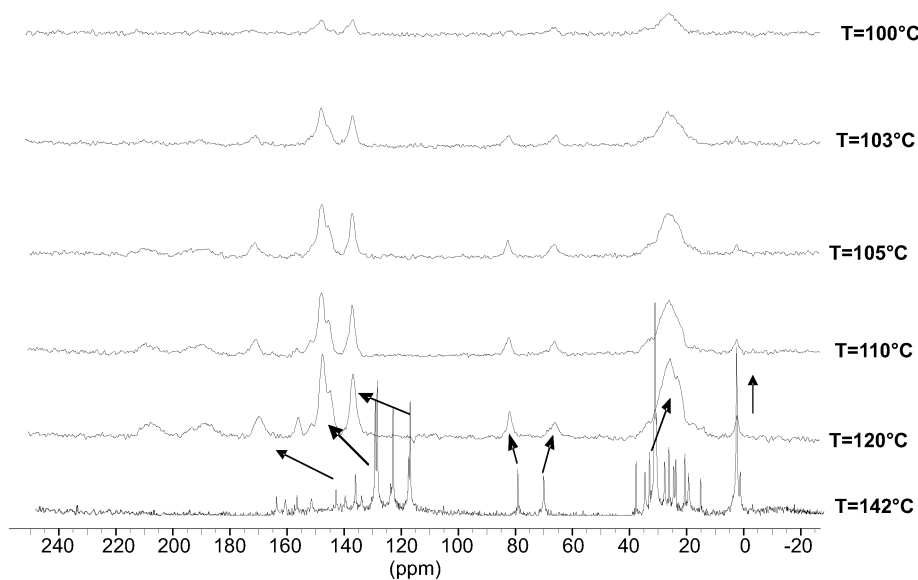


Figure 3. Temperature dependence of the proton-decoupled ^{13}C NMR spectra of BR162A at 125.7 MHz resonance frequency. For signal acquisition, a simple $\pi/2$ pulse sequence is used (no cross polarization), and broad band proton decoupling was performed by rf irradiation.

smectic phases, the information extracted from the line shift of each individual carbon site in the mesogenic core should be equivalent.

The assignment of the lines in the smectic spectra has been performed on the basis of known chemical shift anisotropies of comparable aromatic cores [19–23], and evaluation of the line intensities. The labelling of the aromatic carbons is indicated in figure 4 (top). The *para*

ring sites (1, 4, 5, 8, 9, 12) each contain a single carbon atom per mesogen, their chemical shift anisotropy is very large, and the lines are rather broad and very weak in intensity in the smectic phases. The *ortho* positions (2, 3, 6, 7) are each occupied by two chemically equivalent carbons, except for those in the third ring C (positions 10, 11, 10', 11'), and they have consequently twice the intensity of the *para* positions. *Ortho* positions in ring C

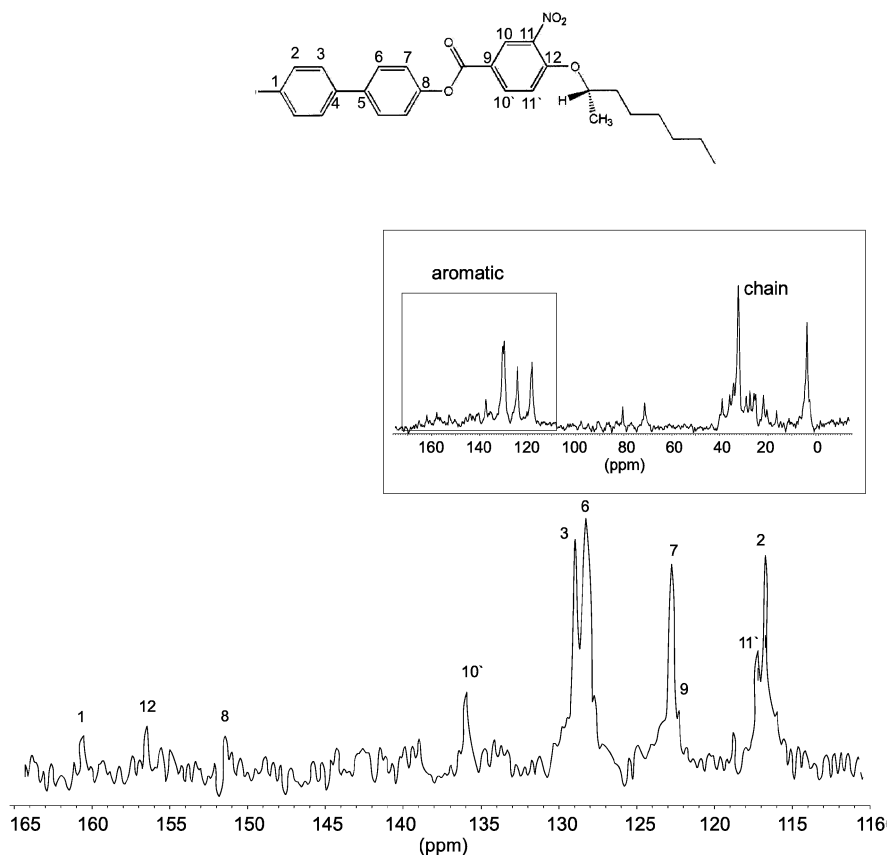


Figure 4. Proton-decoupled isotropic ^{13}C NMR spectrum of BR162A, measured with a $\pi/2$ pulse sequence at the ^{13}C resonance frequency, the temperature is 142°C . Above the spectrum, the assignment of the individual carbon sites 1...12 is indicated.

are not chemically equivalent, and only positions (10', 11') can be identified in the spectra, while (10) and (11) are broadened by the interactions with nitrogen. The chemical shift tensors of the *ortho* carbons are partially averaged by fast ring rotations around the *para* axes, consequently the chemical shift anisotropy in the molecular frame is reduced to about 1/3 of the anisotropy of the *para* carbon sites. These *ortho* positions form the basis of our subsequent evaluation of the spectra.

Before evaluating the spectra further in detail, we tested the orientation of the samples in the spectrometer field. The conventional technique to prepare oriented NMR samples is cooling from the isotropic state through a nematic phase in which the director aligns in the direction of the spectrometer field. This technique is not applicable to BR162A which lacks a nematic phase. Nevertheless, the magnetic field of the spectrometer is sufficient to align the smectic material. Figure 5 shows spectra that have been measured after the sample was simply heated from the crystalline state into the SmC* phase. In the crystalline state, the director and layer orientations in the material are assumed to be

random. The relatively sharp lines of the *ortho* positions (in the centre of the spectra) provide evidence that the SmC* sample is aligned by the magnetic field, even when the sample has not been previously heated into the isotropic phase. The peak positions correspond to an orientation parallel to the \mathbf{B}_0 field of the spectrometer (the magnetic susceptibility anisotropy $\Delta\chi$ is positive). Moreover, figure 5 shows that the smectic material realigns along the magnetic field direction if the sample tube is rotated to a new position. The three spectra were recorded in three different orientations of the sample tube, we waited for about 0.5 h after each reorientation of the sample before the next measurement was started. In all cases, the spectra look very similar, i.e. the layer structure is reorganized by the magnetic interactions of the spectrometer's magnetic field \mathbf{B}_0 with the director. Nevertheless, the alignment is not perfect, and the director distribution, with half-width of approximately 20° around the magnetic field direction, broadens the lines proportionally to their chemical shift anisotropy. Thus, the weakly anisotropic chain lines remain rather sharp while the lines of the *para* positions (left wing of the spectrum) are

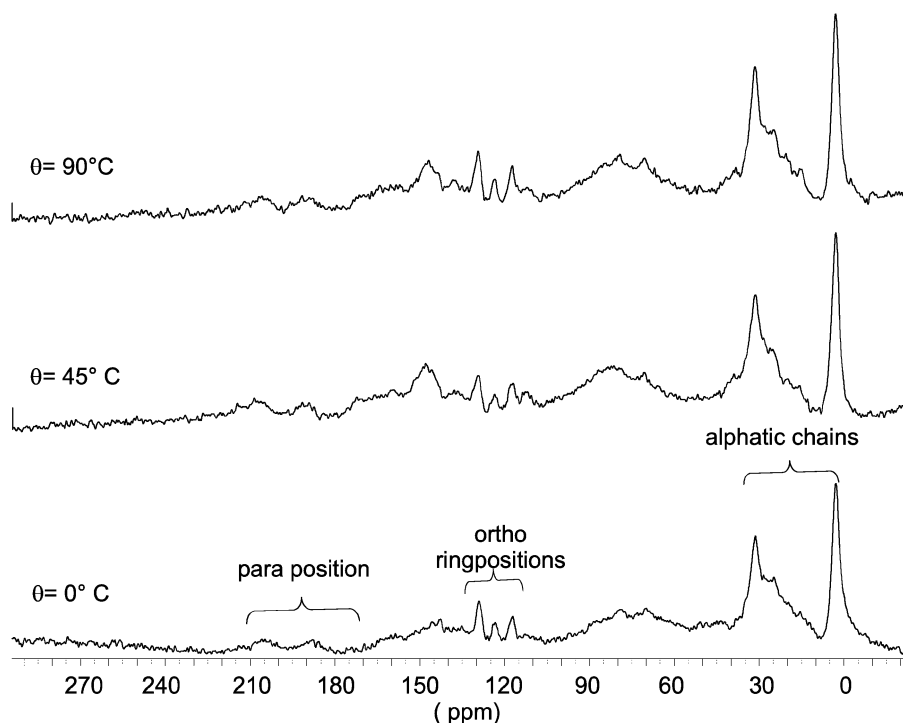


Figure 5. Angular dependence of the ^{13}C NMR spectra of BR162A at 120°C in the SmA phase. The spectra were recorded with time intervals >1 h. It is clear that the material realigns to the magnetic field direction after a sample flip; in particular, the positions of all *ortho* ring positions that are clearly resolved in the middle of the spectrum keep their positions and shapes.

considerably smeared out. The realignment of the material, unfortunately, prevents the measurement of more than one component of the order matrix.

In the following measurements, an optimum sample alignment was achieved by heating the material to the isotropic state and cooling slowly into the SmA phase. This results in a faster and better orientation than by directly heating into the smectic state from the random crystalline powder. The chemical shift of carbon site i in the spectrum depends on the averaged component of the shift tensor. The line positions are given by

$$\nu^{(i)} = \nu_a^{(i)} + \nu_{\text{iso}}^{(i)}$$

where $\nu_{\text{iso}}^{(i)} = \nu_{\text{ref}} - \nu_0 \delta_{\text{iso}}^{(i)}$ is the resonance frequency in the isotropic phase, ν_{ref} is the reference frequency (relative to TMS), $\nu_0 = \gamma B_0 / 2\pi$ is the Larmor frequency of 125.7 MHz and $\delta_{\text{iso}}^{(i)}$ is the isotropic part of the respective chemical shift tensor.

The values of $\nu_a^{(i)} = -\nu_0 \delta_{zz}^{(i)}$ depend on the anisotropic parts of the shift tensors, $\delta_{ij}^{(i)}$, the orientation of their principal axis systems (PAS) in the molecular frame, on the ordering matrix (i.e. time-averaged orientation of the molecular frame within the director frame) and on the orientation of the director frame with respect to the magnetic field \mathbf{B}_0 in the z -direction. For the interpretation

of our spectra, we use the standard approximation of separate averaging of order fluctuations. We assume a fixed orientation of the averaged molecular frame relative to the rings A and B; the long axes of the mesogenic units are nearly parallel to the *para*-axes in the liquid crystalline phases. This molecular frame is taken as the PAS for the order matrix. The resonance frequency of an individual carbon line is then given by

$$\delta_{zz}^{(i)} = S \delta_{\zeta\zeta}^{(i)} \frac{1}{2} \langle 3 \cos^2 \varepsilon - 1 \rangle \frac{1}{2} (3 \cos \phi - 1) \quad (1)$$

where ε is the angle between the director and the orientation of the mesogen long axis (zero in conventional SmA and SmC phases, and equal to the molecular tilt in the de Vries SmA phase), and ϕ is the angle between the director and external magnetic field \mathbf{B}_0 [19]. Brackets denote a time average. In this equation, biaxiality and transversal order are neglected. The $\delta_{\zeta\zeta}^{(i)}$ are the time-averaged tensor components along the molecular long axis ζ in the molecular frame. Values for typical individual aromatic carbon sites in liquid crystal mesogens have been determined earlier, e.g. for the standard material 5CB and similar compounds. Measured chemical shift anisotropies for 5CB and the compound studied here are compared in table 1. Since the positions (2, 3) in ring A and at least positions (5, 6) in ring B have

Table 1. $\delta_{\text{CC}}^{(i)}$ data (in ppm) used for the evaluation of the spectra.

Position	5CB	BR162A (this paper)
1	94	
2	36.7	36
3	37	38
4	89	
5	93	
6	34	36
7	45.4	42.3
8	8.9	
11		35.2
10		52.2

practically the same chemical environment as in the cyanobiphenyl derivative 5CB, they can be directly compared. In position 7, there is already an 8% deviation of the chemical shift tensor anisotropies due to the influence of the cyano group in 5CB.

The transition from the isotropic to the smectic phase occurs within 5 K, in agreement with the proton NMR spectra, but the phase transitions found in the ^{13}C spectra are systematically shifted by 3–4 K. We attribute this to the strong rf irradiation during proton decoupling, which heats the sample, a well known effect in ^{13}C NMR spectroscopy of liquid crystals. In the figures shown later, this offset has been corrected.

The line shifts $\nu_a^{(i)}$ of selected carbon positions respective to their isotropic frequencies have a comparably small temperature dependence in the SmA phase, and a total variation of no more than 25%. A gradual line broadening (see figure 3) with decreasing temperature reveals not only the loss of mobility of the mesogenic units and insufficient decoupling of dipole–dipole interactions, but also the gradual broadening of the director distribution.

The temperature dependent $\nu_a^{(i)}$ are shown in figure 6. Within the SmA phase, they are expected to reflect the order parameter change with temperature. The observed very weak temperature dependence indicates that S remains practically constant, its variation across the SmA temperature range is less than 5%. This is particularly remarkable since X-ray measurements show a considerable layer thickness change in the SmA phase (see, for example [14, 15, 17]). A reduction of the layer thickness with increasing temperature can in principle be caused by a decreasing order parameter with increasing temperature or by an increasing interdigitation of layers at constant order parameter. The NMR data support the latter interpretation.

At the transition to the SmC* phase, the data in figure 6 show a quite unspectacular temperature dependence. There is no pronounced jump at the

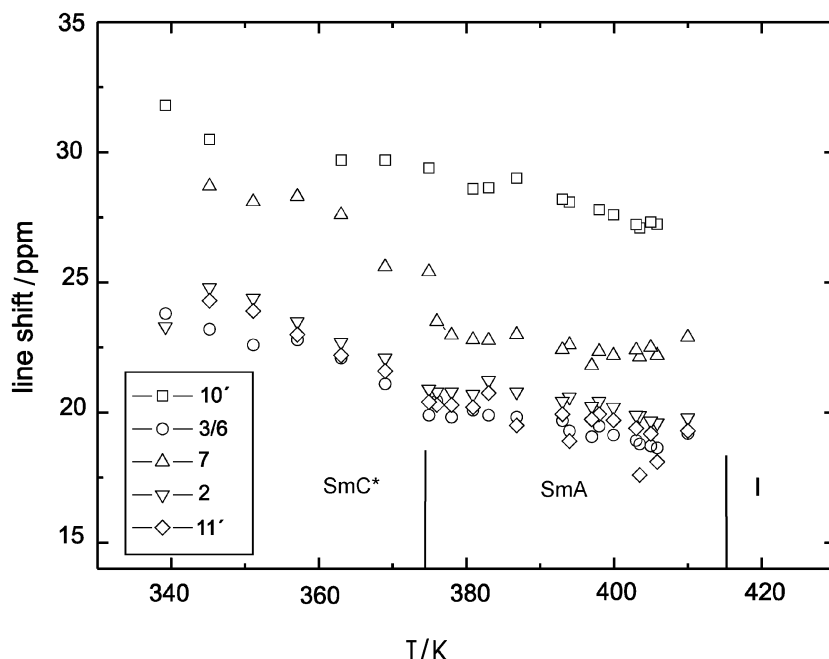


Figure 6. Temperature dependence of the chemical shift anisotropy (line shift with respect to the isotropic position) for some selected positions of the aromatic core of BR162A. We have selected only the sharp, well separated and clearly resolved lines in the spectrum. The accuracy is better than $1 \pm \text{ppm}$. Positions 10' and 11' have only half the intensities of the other lines, their experimental uncertainty is larger than that of the other four positions.

transition to the SmC* phase. The line shifts $\nu_a^{(i)}$ of individual positions respective to the isotropic resonance frequency increase systematically by 5–10%. The temperature characteristics of all lines are qualitatively equal, as is expected for a temperature-independent molecular conformation. Thus, we can concentrate on the evaluation of the most suitable lines for study, 2, 3, 6, and 7. While their positions are almost constant in the SmA phase, the slight increase at the transition as well as the temperature dependence in the SmC* phase have to be discussed. An interpretation of the data has to be performed on the basis of models, since we measure only a product of the phase geometry factor $(3 \cos^2 \varepsilon - 1)/2$, alignment factor $(3 \cos^2 \phi - 1)/2$, and order parameter S , and it is impossible to discriminate these contributions unambiguously in the NMR spectra.

4. Model and interpretation

Figures 7 and 8 show four possible scenarios for the molecular order and alignment at the smectic A–C transition. In a conventional SmA phase as well as in a SmC* phase, $\varepsilon = 0$. If, however, the SmA phase is of de Vries type, then the average mesogen orientation respective to the director is tilted, $\varepsilon \neq 0$. Furthermore, we have concluded from figure 5 that the director realigns in the spectrometer field, so that we can set $\phi = 0$

in equation (1), or at least assume a narrow distribution of the director around the field direction, with its maximum at $\phi = 0$.

First we consider the transition from an oriented conventional SmA phase into the SmC* phase. This is the standard situation. In earlier experiments it was established that in most smectic A–C* transitions of low molecular mass smectogens, the *director* orientation of NMR bulk samples is preserved, figure 7(a). The layers realign on a cone around the magnetic field, establishing the smectic tilt angle to the director. In this case, the temperature dependence of the ^{13}C lines will be smooth and without significant peculiarities at the phase transition. A second scenario, figure 7(b), is the transition of a conventional SmA phase into a SmC* phase with preservation of the *layer* orientation. In that case, the $\nu_a^{(i)}$ would drop across the transition from the smectic A to C* phase and the aromatic line would shift towards the isotropic positions. This can occur either gradually with increasing tilt angle, or immediately if the transition is first order and the tilt angle is discontinuous at the phase transition. This situation of a preserved layer orientation may be found, for example, if a chiral material has a very short pitch that is not unwound by the magnetic field. When $\Delta\chi > 0$, the susceptibility is larger along the pitch than on average perpendicular to it (for reasonable tilt angles, below 54°), and the pitch has a tendency to align in the

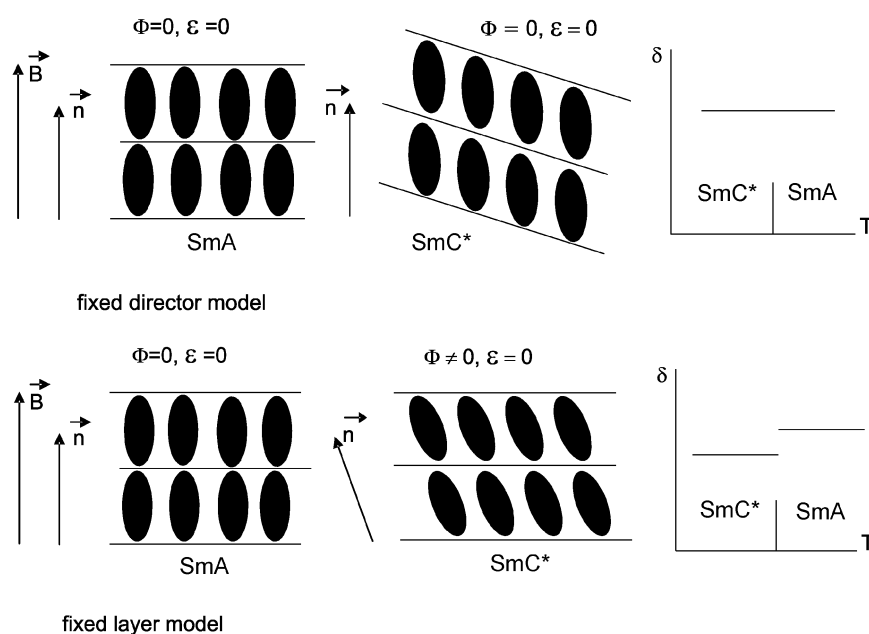


Figure 7. Sketch of the molecular orientations and layer orientations in an ordinary SmA phase at the transition to a SmC* phase with preservation of (a) the director and (b) layers. The sketches on the right hand side show qualitatively the ^{13}C line positions near the transition, with the simplifying assumption of a jump of the smectic tilt angle at the transition to the SmC* phase (see, however, figure 9).

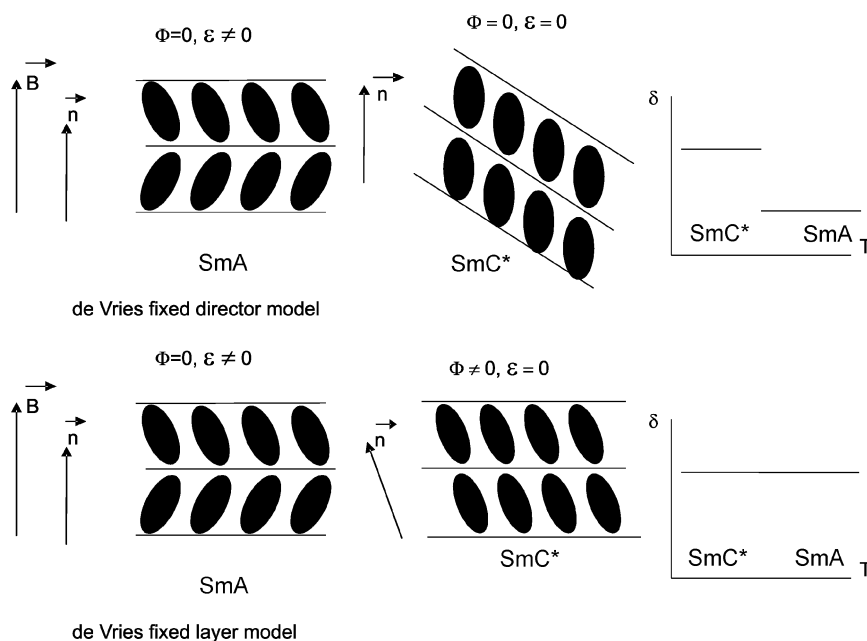


Figure 8. The same as figure 7 but for a de Vries SmA phase, transition into a SmC* phase with preservation of (a) the director and (b) layers. The tilt azimuth of neighbouring layers is not correlated in the SmA phase.

magnetic field direction. In the case shown in figure 7(b), if we equate ϕ to the known optical tilt angle of materials comparable to BR162A [24], a change as shown in figure 9 would be expected, with a 15% drop of $v_a^{(i)}$ across the transition.

Figure 8 shows the two scenarios for a de Vries type SmA phase. In this case, the director is parallel to B_0 in the SmA phase, while the mesogens are distributed on a cone, and $\epsilon \neq 0$. The cone angle in an ideal de Vries phase may be comparable to the tilt angle in the SmC*

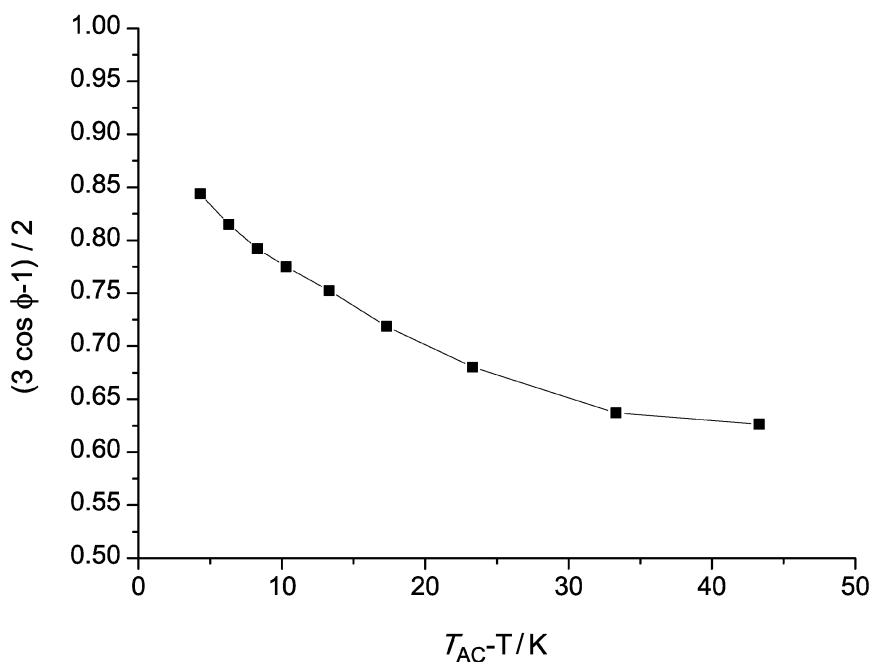


Figure 9. Expected temperature dependence of the factor $(3 \cos^2 \phi - 1) / 2$ if ϕ is set equal to the (optical) tilt angle of the smectic C* phase [17, 24], with the structure model of figure 7(b). Lines guide the eye.

phase far from the transition. If the *director* orientation were preserved at the transition into the tilted phase, the factor $\langle 3 \cos^2 \varepsilon - 1 \rangle / 2$ would change (continuously or discontinuously). The $v_a^{(i)}$ would grow at the transition from the SmA to SmC* phase. On the other hand, if the *layer* orientation were preserved, the line positions would remain almost uninfluenced by the transition. However, this seems unrealistic in the 11.7 T magnetic field, and is in conflict with the conclusions from figure 5.

It should be mentioned that a similar effect as sketched in figure 8(a) has been reported, for comparison, in a synclinic to anticlinic SmC phase transition [19] of a hockey-stick shaped low molecular mass mesogen. There, the diamagnetic susceptibility tensor in the anticlinic phase (alternating tilt azimuth of adjacent layers) has its largest value along the smectic layer normal, the molecular orientation in the director frame is $\varepsilon \neq 0$, and layers align perpendicular to the field \mathbf{B}_0 . In the synclinic phase (same tilt azimuth in adjacent layers), the average mesogen long axes are along the director, and $\phi = \varepsilon = 0$. Such a transition is clearly detectable in the ^{13}C spectra [19], and for an ideal de Vries phase one would expect similar NMR data.

From the known anisotropy of the tensor values $\delta_{\zeta\zeta}^{(i)}$ (table 1), one can estimate the order parameter in the SmA and SmC* phases. The resulting curve is shown in figure 10, where S has been determined from equation (1) as an average of all lines of figure 6, assuming $\varepsilon = 0$ and $\phi = 0$. The order parameter extracted from the *ortho* carbon sites is between 0.52 and 0.56 in the SmA phase. For conventional smectics, this value is rather small. If we assume, for example, $\varepsilon = 20^\circ$ in a de Vries phase, then S would be between 0.64 and 0.68. These

values are still rather low for smectic materials, but probably more realistic.

If the material forms an ideal de Vries phase, i.e. if the optical tilt angle is simply an effect of the random azimuthal ordering of the mesogens on the tilt cone [18], then the NMR lines should have a much more pronounced temperature dependence below the transition from the SmA to the SmC* phase than that actually observed. The reduction of the line shift in the SmA phase would be given by $\langle 3 \cos^2 \varepsilon - 1 \rangle / 2$, with ε equal to the tilt in the SmC* phase. This ideal de Vries scenario can be clearly excluded. The actual change of the chemical shift anisotropy is less than 10%. The NMR measurements are compatible with a weak molecular tilt in the SmA phase, but ε changes only from less than 15° in the SmA to zero in the SmC* phase. Figure 10 would have to be interpreted thus: in the SmA phase, the factor $\langle 3 \cos^2 \varepsilon - 1 \rangle / 2$ is ~ 0.9 or higher. The mesogenic (azimuthally uncorrelated) tilt is less than 15° in the SmA phase, and the order parameter S is close to 0.6. All these quantities have only a very weak temperature dependence in the SmA phase (see figure 10), and the SmA order parameter is approximately equal to that in the SmC* phase.

This interpretation is in qualitative agreement with the X-ray results presented in [17]. An ideal de Vries phase should have a temperature-independent smectic layer thickness, whereas in ordinary smectic A-C transitions, the layers shrink with increasing tilt angle in the SmC phase. In fact, the observed smectic layer thickness has a bend at the transition and decays with decreasing temperature in the smectic C* phase [14, 15, 17], but are weakly than expected from the optical tilt data.

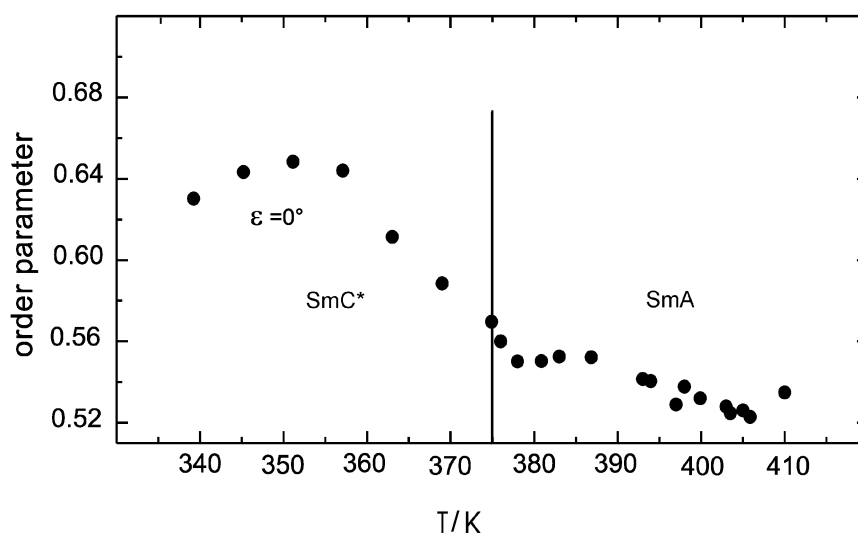


Figure 10. Order parameter extracted from the ^{13}C NMR lines of the *ortho* carbon positions with the assumptions $\varepsilon = 0$ and $\varepsilon = 20^\circ$.

5. Summary

In summary, the orientation and order parameter of the polymer BR162A has been investigated by NMR. This polymer forms the basic building block for the preparation of LC elastomers that have previously been extensively investigated (e.g. [9–18]), and we assume that the basic characteristics of the polymer can be used to understand the structural properties of the respective elastomers.

We find that at the transition into the smectic C* phase, there is only a very small change of the selected aromatic carbon peak positions in the proton-decoupled ^{13}C NMR spectra. This indicates that the material does not form an ideal de Vries smectic A phase, where the smectic A–C transition is just the appearance of azimuthal order of the mesogenic units at constant tilt. The NMR data are only compatible with a small molecular tilt (less than 15°) and random azimuthal order in the SmA phase. The SmA–SmC transition is largely the effect of the change of the polar tilt angle change. We have to conclude that the optical tilt angle [24] is related, to a great extent, to the actual change of the molecular tilt with respect to the layers. This interpretation is in agreement with measurements of the electroclinic effect in [9], where the electrically induced layer shrinkage at the SmA–SmC* transition was studied by means of optical reflectometry. It was found in [9] that the data are consistent with the observed optical tilt angle susceptibility [24] in lateral electric fields.

With this model of weakly or not tilted mesogens in the SmA phase, the order parameter measured by ^{13}C NMR varies over the complete temperature range of the smectic phases by less than 10%. This means that the change of the smectic layer thickness in the SmA phase observed in X-ray measurements [14, 15, 17] cannot be explained by a dramatically decaying order parameter towards the clearing point, but has to be attributed to an increasing interdigitation of the layers or other structural changes.

While the results of this study definitely exclude a large mesogenic tilt in the SmA phase, the NMR data alone cannot unambiguously be interpreted in favour of the existence of a small tilt in that phase. The observed small change of the ^{13}C line positions could be explained alternatively by a slight order parameter change ($\sim 10\%$) across the transition and the ^{13}C NMR data are even consistent with a conventional smectic A–C phase transition.

Acknowledgements

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