Dielectric Investigations in Smectic B-Phases

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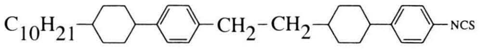
Several liquid crystalline substances exhibiting S_B-phases have been investigated by dielectric and calorimetric measurements. Special attention is taken to the low frequency relaxation process at the phase transition nematic-S_B. From the large change of relaxation frequencies, crystallinity of the S_B-phases has been concluded. Nevertheless, motion is still present and not frozen.

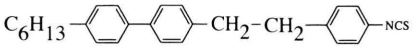
Key words: Smectic B-phase, Dielectric constant, Relaxation frequency, Transition entropy.

Introduction

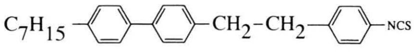
Since the early eighties it has been knowning that there are different types of smectic B phases [1, 2]. The common feature of these phases is the hexagonal arrangement of molecules which are orthogonal to the layer planes. The hexatic B phase (S_{Bhex}) additionally exhibits a long range bond orientational order [3], whereas the crystalline B phase (S_{Bcryst}) exhibits a long range translational order. They can be distinguished by microscopic investigations coupled with calorimetric measurements [4] or X-ray investigations [5, 6]. To our mind, dielectric spectroscopy is a further suitable method to study and distinguish hexatic and solid like phases. Already 1981–1983 dielectric data of both S_B phases were published [7–9], whereby the more or less abrupt decrease of relaxation frquencies at the transition into the S_B phase was taken as distinguishing feature. In this paper the dielectric properties of seven substances possessing the transition N-S_B are presented. All of them were synthesized by Dabrowski et al. [10–13].



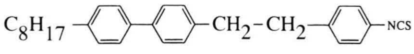
10CBAB-NCS



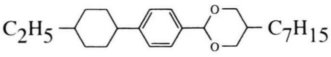
6BBAB-NCS



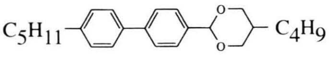
7BBAB-NCS



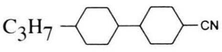
8BBAB-NCS



2CBD7



5BBD4



3CCH

The substances with isothiocyanate groups and dioxane rings belong to homologous series proved to be valuable components of LC mixtures. The phase sequences and transition temperatures were determined by polarisation microscopy with exception of **3CCH**, were we used the DSC-data because of the low transition temperatures. It should be pointed out that specially the last data agree well with the published one [14]. X-ray studies of **2CBD7** and some homologues confirmed the S_{Bcryst} type [15], whereas, the character of S_B in the isothiocyanates has not been classified yet. The trans-4-*n*-alkyl-cyano-bicyclohexanes posses a S_{Bcryst} phase of the bilayer type [16].

The phase transition temperatures in °C and short names are given in Table 1.

Table 1. Phase transition temperatures of investigated substances in Celsius.

Short name	Phase sequence
10CBACB-NCS	K 97 (S_B 96) N 229 I
6BBAB-NCS	K 70 S_B 100 N 132 I
7BBAB-NCS	K 70 S_B 103 N 135 I
8BBAB-NCS	K 60 S_B 104 N 130 I
5BBD4	K 48 S_B 94 N 161 I
3CCH	K 58 (S_2 17 S_1 42 S_B 55) N 79 I*
2CBD7	K 45 S_E 52 S_B 99 N 124 I

* from DSC-measurements.

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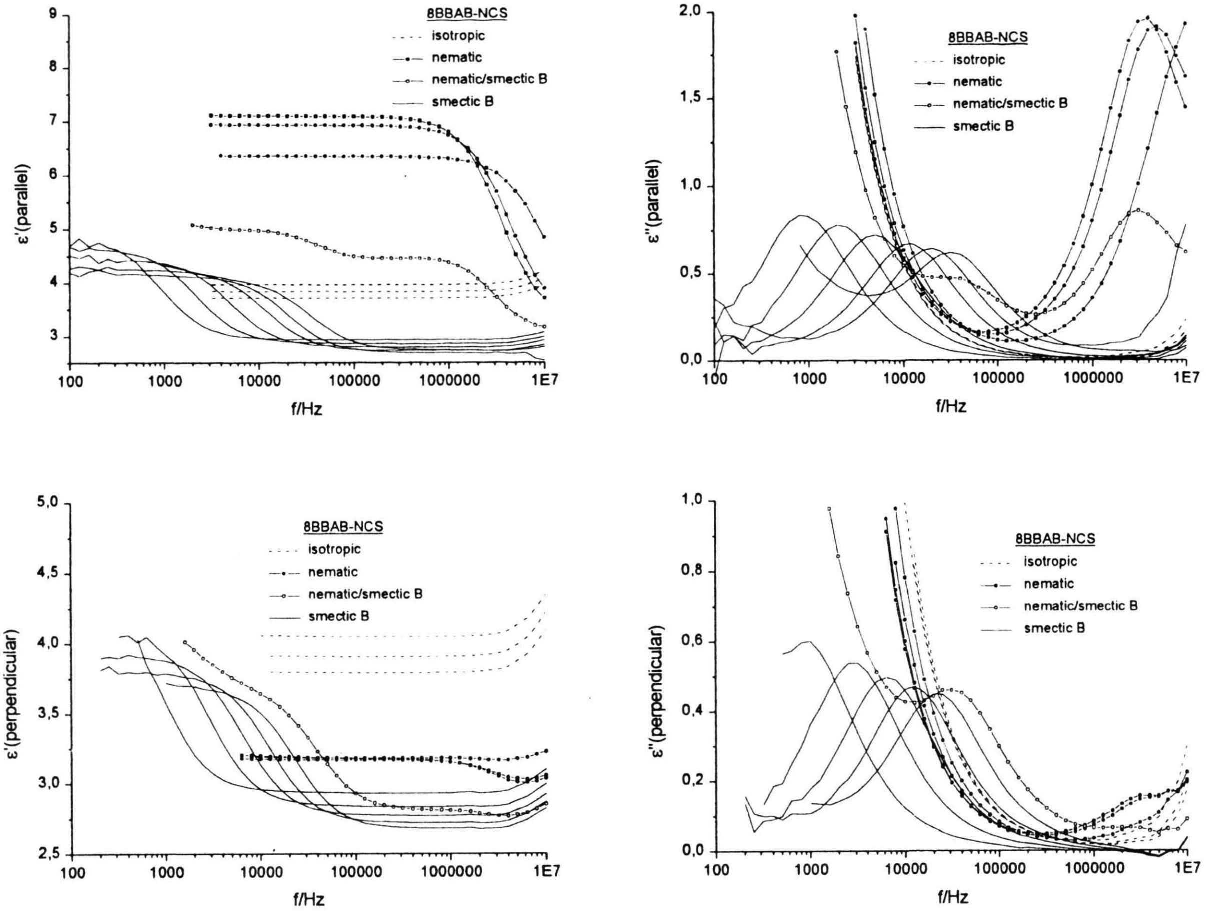

Fig. 1. Experimental curves of **8BBAB-NCS** at different temperatures. Parallel orientation: 150.5 °C, 140.5 °C, 129.4 °C (isotropic); 120.4 °C, 109.6 °C, 105.6 °C, 100.6 °C (nematic); 96.6 °C (two phase range); 88.5 °C, 80.5 °C, 68.4 °C, 56.4 °C, 44.4 °C (smectic B). Perpendicular orientation: 150.1 °C, 140.8 °C, 128.3 °C (isotropic); 119.2 °C, 110.2 °C, 105.0 °C, 102.9 °C (nematic); 98.2 °C (two phase range); 89.7 °C, 80.5 °C, 70.8 °C, 58.9 °C, 42.2 °C (smectic B)

Experimental

Dielectric measurements were carried out using a HP 4192A impedance analyzer (100 Hz–10 MHz) and at low frequencies a Solartron Schlumberger SI 1260 together with a Chelsea Dielectric Interface. Details of the experimental technique are published in [16, 17].

For demonstration some measured curves of the dielectric constant ε' and dielectric loss ε'' for **8BBAB-NCS** are given in Figure 1. From the dispersion curves $\varepsilon'(f)$ the static dielectric constants (ε_0, ε_∞) and from the absorption curves $\varepsilon''(f)$ the relaxation frequencies (f_R) have been determined by fitting to the Cole-Cole equation [18].

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\left[1 + \left(\frac{f}{f_R}\right)^h \sin\left(\frac{\pi}{2}(1-h)\right)\right]}{1 + \left(\frac{f}{f_R}\right)^{2h} + 2\left(\frac{f}{f_R}\right)^h \sin\left(\frac{\pi}{2}(1-h)\right)}, \qquad (1)$$

f; f_R – frequency, relaxation frequency, ε', ε'' – dielectric permittivity, dielectric loss, h – Cole-Cole parameter ($h = 1$ for ideal relaxations of the Debye type).

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\left(\frac{f}{f_R}\right)^h \cos\left[\frac{\pi}{2}(1-h)\right]}{1 + \left(\frac{f}{f_R}\right)^{2h} + 2\left(\frac{f}{f_R}\right)^h \sin\left(\frac{\pi}{2}(1-h)\right)} + \frac{A}{f}, \qquad (2)$$

ε_0 – static dielectric constant (low frequency limit),
ε_∞ – high frequency limit of the dielectric constant.

Normally one expects a Debye-behaviour for the low-frequency absorption, but in order to see deviations connected with low-temperature phases this extended expression was used. The disturbing contribution of conductivity to the overall loss has been taken into account by the term Af^{-1}. In order to orient the molecular director in the nematic phase, a magnetic field ($B \approx 0.7$ T) or an electric bias field ($E = 300$ Vcm^{-1}) was applied. Passing the transition N-S_B, the orienting field remained switched on in order to get well oriented domains in S_B, too.

Results and Discussion

Before discussing the results the different experimental procedures should be mentioned. The isothiocyanates have been oriented by the magnetic field and $\varepsilon_{\parallel 01}$ as well as $\varepsilon_{\perp 0}$ could be determined. **7BBAB-NCS** is an exception. Because of the small amount of this substance the brass capacitor could not be filled completely and a glassy sandwich cell has been applied. That's why **7BBAB-NCS** could not be oriented. In the case of **10CBACB-NCS** no data in the isotropic phase have been obtained because of the high clearing point. The dioxane derivative **2CBD7** turned out to be not stable during the measurement in the brass capacitor. Despite of some attempts to a gently procedure the phase transition temperatures dropped down by 8 K every time, while the nematic and smectic B phase kept maintained. That's why the obtained results on **2CBD7** have to be interpreted with care. The **3CCH** compounds has been oriented by the electric field in order to estimate $\varepsilon_{\parallel 0}$. The application of the magnetic field would not be useful because of the low negative anisotropy of the diamagnetic susceptibility. Generally, the index "parallel" is related to that configuration where the electric measuring field is parallel to the nematic director [19] and "0" refers to the low-frequency limit of this dielectric constant.

As already expected all the substances possess the low frequency relaxation in the range 100 Hz–10 MHz resulted from the reorientation of longitudinal dipole moments. In the nematic phase it can be observed as a very intensive Debye absorption at parallel orientation which hints to a good alignment of molecules. In the S_B phase this relaxation process can be detected at parallel as well as perpendicular orientation. This fact will be discussed later.

Figure 2 provides a survey over the temperature dependence of static dielectric constants of some compounds. All of them exhibit a positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel 0} - \varepsilon_{\perp 0}$) caused by the considerable longitudinal dipole moment. The most striking result is the aprupt decrease of $\varepsilon_{\parallel 0}$ at the transition N/S_B. It is not only the consequence of restrictions of dipolar reorientations because in this case $\varepsilon_{\perp 0}$ should also decrease, but it is caused by the loss of the parallel and perpendicular orientation. The detection of the low frequency relaxation at perpendicular orientation in S_B can be taken as proof (see Figure 1). Even the attempt to orient the molecules in the S_B phase by means of a stronger magnetic field (1 T) failed. Why is it so difficult to get oriented molecules in this phase? A reason for that could be the considerable increase of the viscosity in the transition range N/S_B which has been observed during the microscopic investigations. The strength of the magnetic field is not sufficient to orient the statistically oriented clusters of the developing S_B phase.

Let us have a look to the mean dielectric constant $\bar{\varepsilon}_0$. For the derivation of $\bar{\varepsilon}_0$ the following formula, which is valid for uniaxial, has been used [18]: $\bar{\varepsilon}_0 = \frac{1}{2}(\varepsilon_{\parallel 0} + 2\,\varepsilon_{\perp 0})$.

There are only few papers about dielectric constant at the transition into the S_B phase and, to our knowledge, no data about dielectric constants in the S_{Bhex} phase at all. In [20, 21] a decrease of $\bar{\varepsilon}_0$ of 20–25% was found, whereas in [22] only a negligible drop was detected. The rough estimation of the change of $\bar{\varepsilon}_0$ in this substances under investigation provides a sophisticated picture. For **10CBACB-NCS** and **2CBD7** the mean dielectric constant keeps constant, in the isothiocyanates $\bar{\varepsilon}_0$ decreases by 10–20% and **3CCH** exhibits a remarkable change of about 40%. Brückert and Würflinger measured a decrease of $\bar{\varepsilon}_0$ at the transition N/S_B of about 50% for **5CCH** [23].

After fitting the absorption curves to the Cole-Cole equation and estimating the relaxation frequencies from the maxima, the temperature dependence of f_R has been depicted. A summary of the so-called Arrhenius plots is shown in Figure 3. For a better clarity the term $\left(\frac{1}{T} - \frac{1}{T_{N/SB}}\right)$ has been used instead of $\frac{1}{T}$. The results obtained from the relaxation measurements are summarized in Table 2. The listed activation energies have been derived from the slopes of the Arrhenius graphs in the respective phases. The quotient p is a measure for changes of relaxation frequencies at

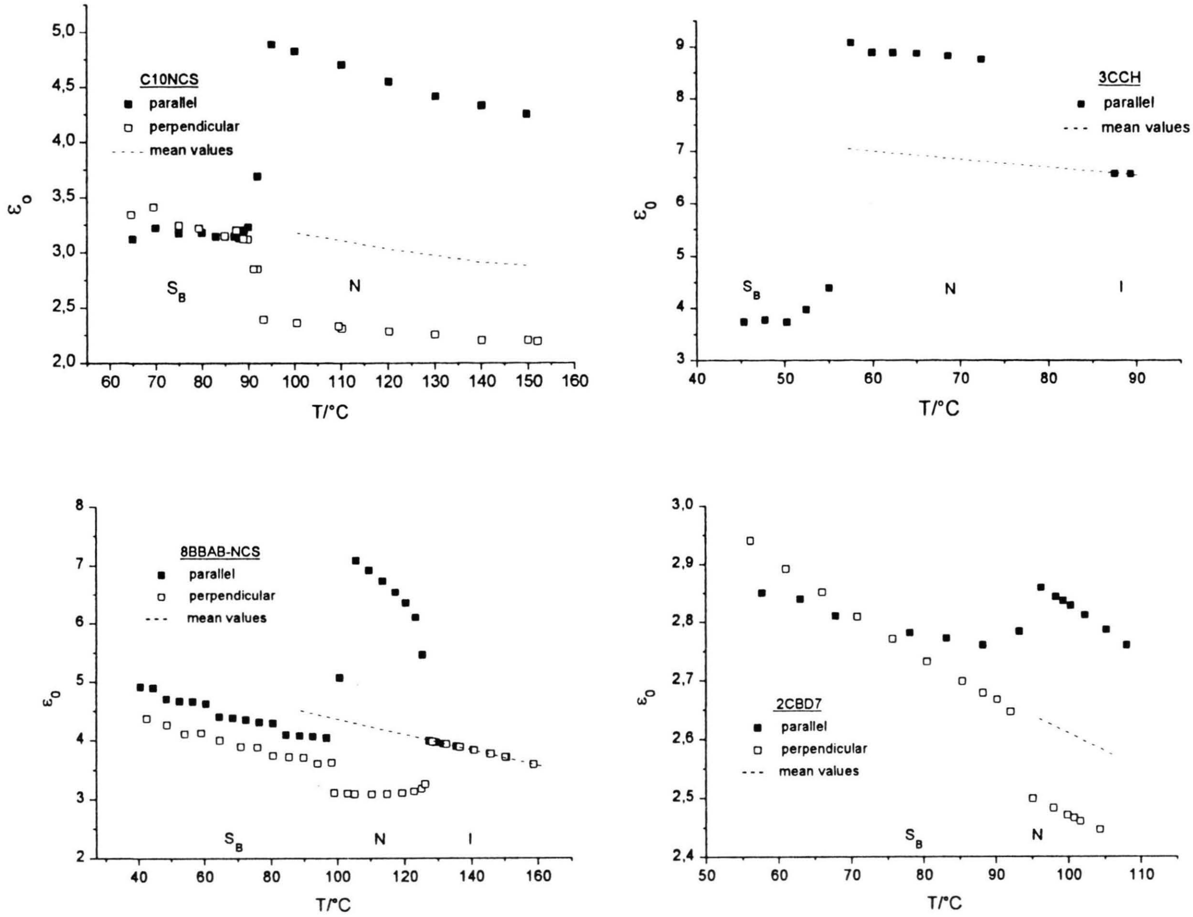

Fig. 2. Temperature dependence of static dielectric constants.

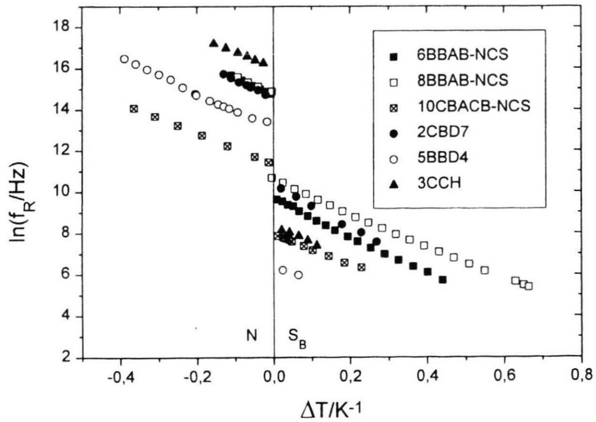

Fig. 3. Arrhenius plots with a normalized scale of the inverse temperatures: $\Delta T = \left(\frac{1}{T} - \frac{1}{T_{N/SB}}\right) \cdot 1000$.

phase transitions and is derived as described in the table. From calorimetric measurements, using a DSC 7 (Perkin Elmer), the phase transition entropies have been estimated and listed in Table 2, too.

It should be mentioned that in the N as well as in the S_B phase the absorption curves can be treated like ideal Debye absorptions. That means, there is a single characteristic relaxation frequency for all of the molecules and no distribution of relaxation frequencies. The considerable drop of f_R at the transition into the S_B phase is the most important result. It amounts from 30 up to 2000. Such a big change of f_R has never been detected before at this transition. In order to prove that we handle with the S_B phase and no crystallization takes place, the DSC scans of **6BBAB-NCS** are shown in Figure 4. The enantiotropic transition N/S_B at about 100 °C can clearly be recognized and be

Table 2. Summary of the dielectric properties at the transition N/S_B.

Substance	$\left(\frac{\Delta\bar{\varepsilon}_0}{\bar{\varepsilon}_0}\right)_{T_{N/SB}} \cdot 100\% \pm 5\%$	$p=\frac{f_R(N)}{f_R(S_B)} \pm 10\%$	ΔS $\mathrm{J\,mol^{-1}\,K^{-1}} \pm 7\%$	E_A (N) $\mathrm{kJ\,mol^{-1}} \pm 5\%$	E_A (S_B) $\mathrm{kJ\,mol^{-1}} \pm 5\%$
10CBACB-NCS	0	30	8	63	60
6BBAB-NCS	20	150	15	72	77
7BBAB-NCS	10	60	14	52	50
8BBAB-NCS	10	60	15	65	65
2CBD7	0	70	16	77	80
5BBD4	–	1000	8	74	–
3CCH	40	2000	14	58	62
5CCH *	50	200	14	77	65

* The data of 5CCH have been taken from [23].

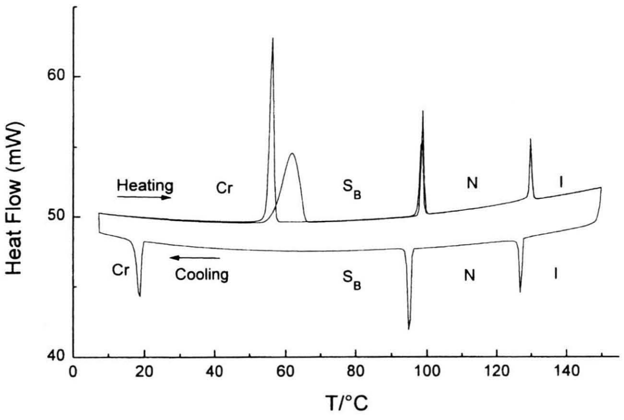

Fig. 4. DSC curves of **6BBAB-NCS**. Rate: 10 K/min; heating–cooling–heating.

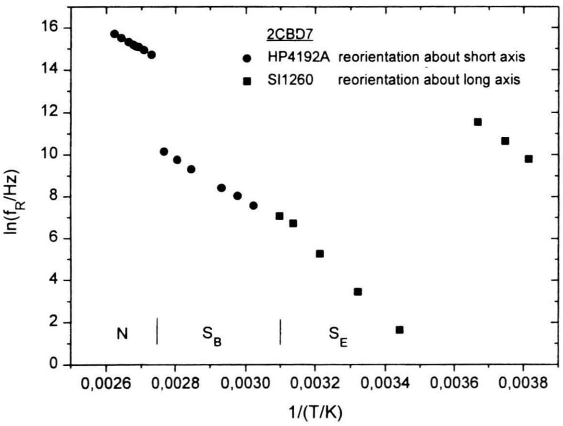

Fig. 5. Temperature dependence of relaxation frequencies of **2CBD7**. By means of the low frequency device SI 1260 the reorientation about the long axis has been detected.

distinguished from the melting and crystallization process. Furthermore, in the solid state normally the dipolar motions are frozen, and therefore no relaxation can be detected.

Following the formerly formulated ideas [9] we conclude that all investigated S_B phase belong to the S_{Bcryst} phase type. There is a relation between the high p values and high transition entropies ΔS [7] which is confirmed by our investigations. The substances possess high transition entropies of about 15 $\mathrm{J\,mol^{-1}\,K^{-1}}$ corresponding to the high p values.

Contrary to the statement of Gouda et al. [21], the molecular rotation around the short axis in S_{Bcryst} phases is not frozen. Even more than that, this relaxation is not only caused by librations but is caused by end over end reorientations of the longitudinal dipole moments, which results from the markable dielectric increments. In order to prove this statement, let us have a look at the dielectric loss of **10CBACB-NCS**. From the temperature dependence of ε_0 (see Fig. 2) a statistical orientation of molecules in the S_B phase can be concluded. In this phase the dielectric loss amounts 0.75. Using the simplified formula of Attard [24] it is possible to calculate the expected loss for the case of a perfectly parallel orientation $\varepsilon''_{\parallel}$:

$$\varepsilon''_{\parallel\,\mathrm{exp}} = \frac{1}{3}\varepsilon''_{\parallel}(1+2S_d) \Rightarrow \varepsilon''_{\parallel} = 2.25\,,$$

Domain order parameter $S_d = 0$ for **C10NCS** in S_B, $\varepsilon''_{\parallel\,\mathrm{exp}} = 0.75$.

The measured dielectric loss of 0.75 for statistically oriented molecules in the S_B phase corresponds to the calculated value 2.25 which indeed really has been measured in the nematic phase. The three dimensional translational order of S_{Bcryst} phases only reduces the f_R of this motion. It is worth mentioning that the activation energies do not increase at the transition N/S_B and that great structural changes do not influence this energy barrier.

Within the available frequency range of 100 Hz–10 MHz no second relaxation process could be detected in the S_B phase. The expected high frequency process caused by reorientations of perpendicular components of the dipole moment does not exhibit a significant drop of f_R. The dioxane derivate possesses a further smectic phase which has been identified as an S_E phase by texture investigations. Because of the chemical instability of the material no reliable results of static dielectric constants in this phase have been obtained. Nevertheless, the relaxation frequencies can be discussed. Looking at the Arrhenius diagram of **2CBD7** (Fig. 5), an increase of the activation energy at the transition S_B/S_E from 80 kJ/mol to 130 kJ/mol can be established. Furthermore, the above mentioned high frequency relaxation has been found with the Cole-Cole parameter $h = 0.5$ and the increment 0.08. In the S_E phase the reorientation around the long molecular axis seems to be more hindered than in the S_B phase, which results from the development of the so-called herringbone structure [25].

Acknowledgements

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