Calorimetric and dielectric investigations of smectic liquid crystals with aerosil

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Two strongly polar 4-(4-cyanobenzyloxy)benzylidene 4-*n*-alkylanilines were synthesized for the first time and mixed with the hydrophilic aerosil A 300. The compounds, showing a rich polymorphism, and the mixtures were investigated by calorimetric and dielectric methods. Phase transitions of first and second order were detected. Neither the phase transition temperatures nor dielectric relaxation times are strongly influenced by addition of aerosil up to 20%.

1. Introduction

The physics of heterogeneous liquid crystals (LCs) is of interest for both applied and fundamental physics [1–3]. One such system is provided by filled LCs consisting of suspensions of aerosil particles in a LC matrix. That such heterogeneous systems could be obtained by mixing liquid crystals with aerosil was demonstrated first by Eidenschink [2]. Such materials give a good opportunity to study changes in physical behaviour especially at phase transitions under restricted geometry. Thereby, samples showing first and second order transitions between different high temperature liquid crystalline phases have been shown to be of interest. High resolution calorimetric investigations have demonstrated a small decrease of the clearing temperature by the addition of aerosil [4–6]. Dielectric measurements have shown an increase of the relaxation frequencies for reorientation about the molecular axis short in the nematic state [7].

The aim of the present investigation is to use calorimetric and dielectric relaxation measurements to monitor different LC phases over a broad temperature range.

2. Experimental

2.1. *Materials*

The hydrophilic aerosil A 300 was obtained from Degussa. The diameter of the particles was about 7 nm. AFM measurements on a heterogeneous mixture with a polymer liquid crystal have shown that the aerosil particles form 40–250 nm sized aggregates which are

building units for bigger agglomerates [8]. In this way the aerosil particles are not homogeneously distributed in the mixture.

With regard to the dielectric measurements, samples with strong terminal dipole moments are necessary. For this reason two new homologous 4-(4-cyanobenzyloxy)-benzylidene-4-*n*-alkylanilines were synethesized:
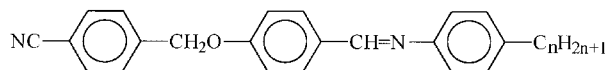
$n = 8$: Cr (SmX1 77.5) 82 SmC 112.5 SmA 144.2 N 166.2 I   **S8**
$n = 14$: Cr 73 SmX2 79 SmX1 89 SmC 98 SmA 165 I   **S14**

SmX1 and SmX2 are low temperature smectic phases identified only by texture observations.

The compounds were prepared by condensation of appropriate 4-*n*-alkylanilines with 4-(4-cyanobenzyloxy)-benzaldehyde in ethanol. The last mentioned benzylether was obtained by reaction of 4-hydroxybenzaldehyde with 4-cyanobenzyl bromide. The final products were recrystallized from ethanol and at least once from a mixture of toluene and heptane in order to reduce the conductivity. The phase transition temperatures (in °C) and the phases given above were determined by polarizing microscopy.

Both compounds were mixed with aerosil in the solid state, heated to the isotropic phase and again continuously mixed in order to get a homogeneous sample. This procedure was restricted to 5 min to avoid decomposition of the samples.

2.2. *Techniques*

Calorimetric investigations were made with a Perkin-Elmer DSC 7. These measurements were especially

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necessary for samples containing higher concentrations of aerosil, because in these cases phase transitions could not be readily detected by the microscopic method. The transition enthalpies were related to 1 g of the respective liquid crystalline sample.

Dielectric measurements were carried out using a micro-capacitor consisting of two glass plates ($d = 0.050$ mm, $A = 1$ cm^2) and the frequency range from 100 Hz to 10 MHz was covered using the HP 4192A Impedance Analyzer. The glass plates were coated on one side with gold. The cell was calibrated using cyclohexane before any measurements. The temperature was controlled by a Eurotherm regulator. Compound **S8** could be easily oriented in an external magnetic field of 0.7 T. A bias voltage of 35 V did not shift the relaxation frequency, but in this case the conductivity was smaller.

The samples containing aerosil were very viscous. Therefore, they were first put on one of the glass plates with two spacers; the second glass plate was then pressed down on the first plate. In this way only approximate values of the dielectric constant could be obtained by using the same calibration constant. It should be pointed out that the relaxation frequencies and the Cole–Cole distribution parameters are not influenced by this technique.

3. Results and discussion
3.1. *Pure components*

The phase transitions of the pure compounds, excluding the melting process, are reversible as found by calorimetric measurements. Static dielectric constants of **S8** are given in figure 1. The data were calculated from the real part of equation (1) which will be discussed later. There is only a small change in $\varepsilon_{\perp 0}$ at 78°C indicating the existence of a supercooled smectic phase; $\varepsilon_{\parallel 0}$ decreases on cooling after reaching a maximum in the nematic state. This indicates a strong dipole correlation in the direction of the molecular long axis [9]. The relaxation time according to equation (1) increases step-wise at the SmC–SmX1 transition. This process is then followed by a decrease of $\varepsilon_{\parallel 0}$ (and also of $\varepsilon_{\perp 0}$) to about 2.3, a classical value of a solid phase. The approximate value of the relaxation time in the SmX1 modification is not given in figure 5 because the mixture of **S8** with aerosil could not be supercooled. **S14** could not be oriented by an external magnetic field. The given dielectric constants in figure 1 are nearly $\varepsilon_{\perp 0}$ values due to the spontaneous orientation of the sample. In this case the SmC–SmX1 and the SmX1–SmX2 transitions can be clearly seen. A few degrees after the last mentioned transition the sample crystallizes. It should be pointed out that the dielectric constants $\varepsilon_{\perp} > 2.5$ in the low temperature phases prove the existence of fast dynamics
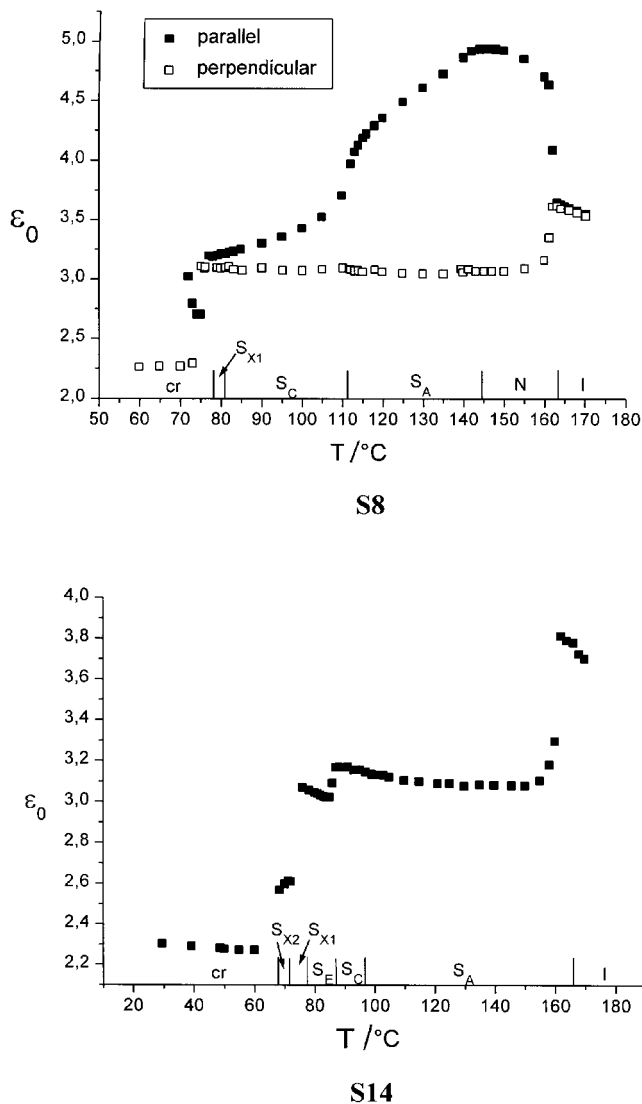

S8

S14

Figure 1.   Static dielectric constants of the pure samples at different temperatures.

and, together with the reversibility of the phase transitions, the existence of smectic phases at lower temperatures.

3.2. *Calorimetric studies*

Calorimetric measurements were carried out for the pure LC samples and mixtures containing up to 20% by weight of aerosil. The data obtained are listed in table 1. From this table it is clear that no significant change occurs in either the temperatures or the corresponding transition enthalpies, excluding the melting process, for all the investigated aerosil concentrations. As expected, stronger changes are observed, particularly in the enthalpy values, if a solid phase is involved in the transition. This indicates the formation of metastable solid phases. For illustration, DSC traces of **S14** at the SmA–SmC transition with a very high resolution are

Table 1. Phase transition temperatures (°C) and enthalpies (in brackets, $J\,g^{-1}$) related to 1 g of the LC sample (in brackets) for **S8**, **S14** and different aerosil (wt %) mixtures.

Transition	wt % aerosil				
	0	5	10	15	20
S8					
N–I	165.6	165.5	166.2	166.1	165.7
	(5.8)	(5.3)	(6.1)	(5.9)	(5.8)
SmA–N	144.2	144.0	144.5	144.6	143.5
	(0.04)	(0.03)	(0.09)	(0.02)	(0.04)
SmC–SmA	112.7	113.5	113.6	113.6	113.4
	(1.4)	(1.3)	(1.1)	(1.3)	(1.1)
Cr–SmC	83.1	80.5	83.9	83.8	82.3
	(38.6)	(25.1)	(34.2)	(34.0)	(30.5)
S14					
SmA–I	165.0	164.7	165.5	164.7	165.0
	(16.5)	(13.3)	(15.9)	(14.7)	(15,.)
SmX1–SmC	88.9	88.6	89.3	88.6	88.6
	(10.0)	(8.7)	(10.9)	(9.7)	(9.8)
SmX2–SmX1	79.7	79.0	80.0	79.0	78.8
	(29.2)	(14.8)	(20.5)	(17.6)	(17.7)
Cr–SmX2	72.9	69.3	70.6	69.3	69.0
	(45.5)	(33.8)	(22.1)	(7.5)	(3.3)

presented in figure 2. In contrast to **S8**, where a small transition peak occurs, in **S14** only a step in c_P is observed. This reflects a clear second order transition. Within experimental error, no change of the transition temperatures and enthalpies by adding 10% aerosil is seen. It was difficult to detect this transition by DSC measurements. For this reason no data are given in table 1 for this transition in **S14**.

3.3. *Dielectric studies*

Measured dielectric losses ε' and fitted curves for **S8** are given in figures 3 and 4 as a function of frequency f. The data were fitted to the imaginary part of the modified Cole–Cole equation:

$$\varepsilon^* = \frac{iA}{f^N} + \left[\varepsilon_1 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau)^{1-\alpha}} \right] + Bf^M \qquad (1)$$

where ε_1 is the high frequency limit of the dielectric constant, $\varepsilon_0 - \varepsilon_1$ is the dielectric increment, τ the relaxation time and α the Cole–Cole distribution parameter. A, N provide for a description of the conductivity; B, M take account of resonance effects at high frequencies.

The detected dielectric absorption is related to the reorientation of the molecules about their short axes. It is important that this motion reflects indirectly the order in the phase [10]. The calculated relaxation times versus the reciprocal temperature are given in figures 5 and 6. The mean values of the Cole–Cole distribution parameters of a sample at different temperatures are practically constant. The respective data are listed in table 2.

Table 2. Cole–Cole distribution parameters of the investigated samples: error ± 0.02.

Sample	wt % aerosil		
	0	10	20
S8	0.00	0.04	0.06
S14	0.00	0.08	0.08

4. Conclusions

Summarizing the experimental results we can say:

(1) Addition of aerosil results in a small decrease of the relaxation times of **S8**. The activation energies for the relaxation times of about $64 \pm 2\,kJ\,mol^{-1}$ (SmA) and $90 \pm 2\,kJ\,mol^{-1}$ (SmC) of the pure sample are not changed.

(2) Aerosil has practically no influence on the relaxation times and activation parameters ($E_A = 74 \pm 2\,kJ\,mol^{-1}$ in the SmA phase) of **S14**. The dynamics do not change at the second order transition SmA–SmC.

(3) The increase of the Cole–Cole distribution parameter with increasing concentration of aerosil may indicate the influence of the surface on the dynamics.

It should be considered that a small decrease in the relaxation time could occur if there is a slight decomposition of the sample during mixing with aerosil and filling of the measuring cell. From the data obtained we can however say that addition of relatively large
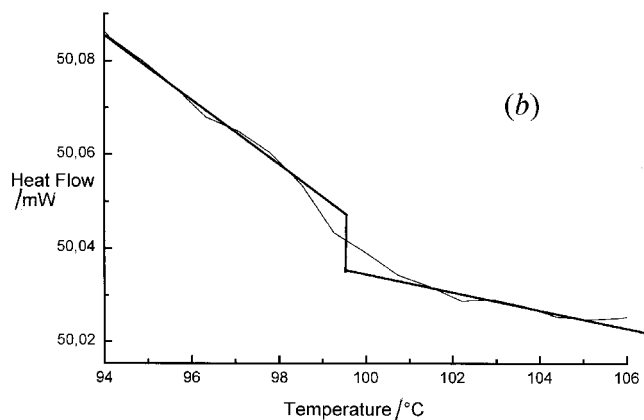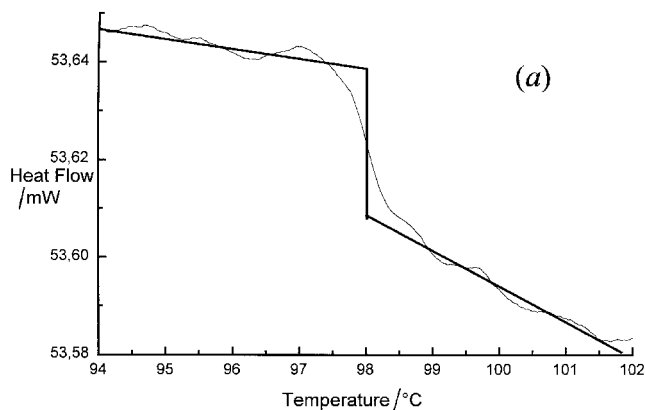
(*a*)

(*b*)

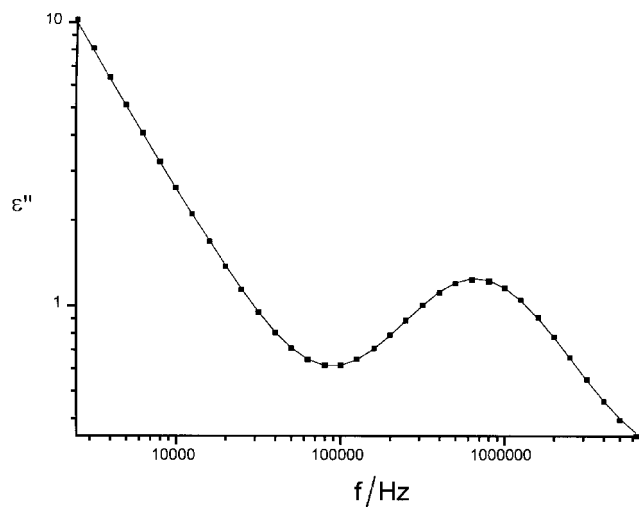Figure 2.   DSC traces of **S14**: (*a*) without aerosil, (*b*) with 10 wt % aerosil.

Figure 3.   Measured loss and fitted curves for **S8** parallel to the nematic director at 95°C. Fit parameters: $\varepsilon_0 = 3.36$; $\varepsilon_1 = 2.35$; $\tau = 8.749 \times 10^{-7}$ s; $\alpha = 0$.
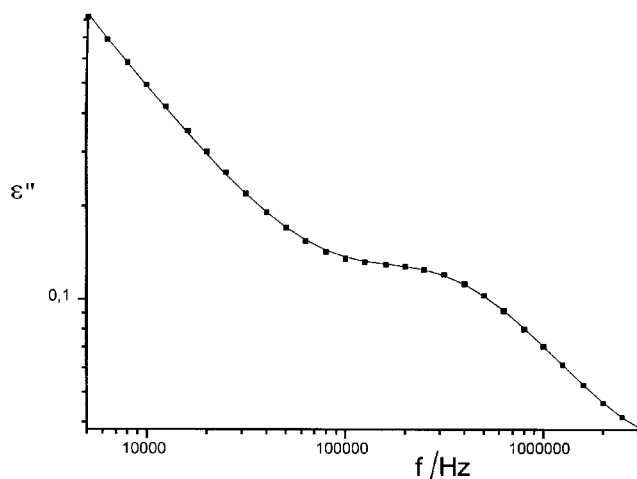

Figure 4.   Loss of **S8/20** containing 20 wt % of aerosil at 95°C. Fit parameters: $\varepsilon_0 = 1.60$; $\varepsilon_1 = 1.50$; $\tau = 7.486 \times 10^{-7}$ s; $\alpha = 0.08$.
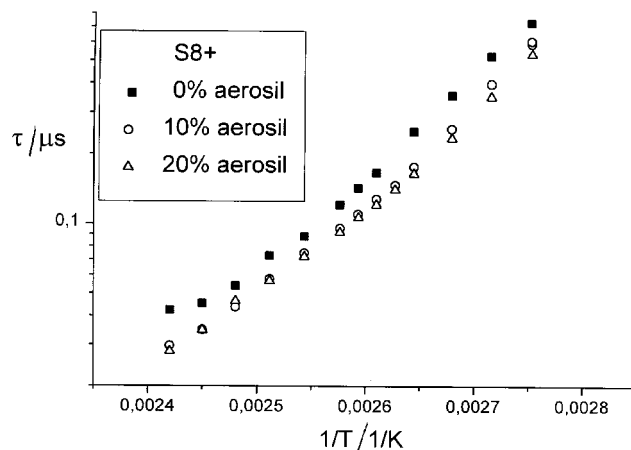

Figure 5.   Relaxation times of sample **S8** and mixtures with 10 and 20 wt % aerosil.
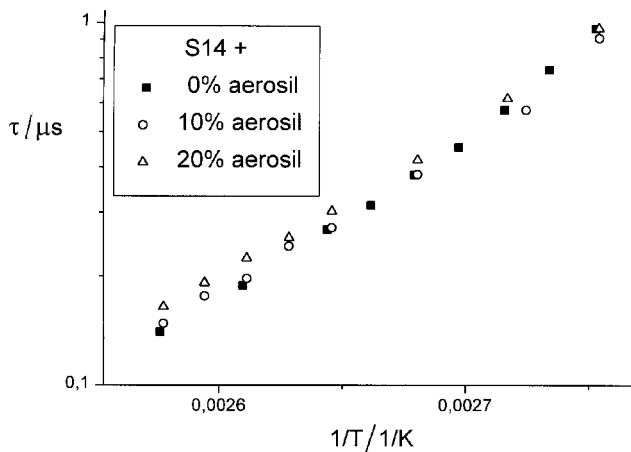

Figure 6.   Relaxation times of **S14** and the respective mixtures containing 10 and 20 wt % aerosil.

amounts of aerosil to a liquid crystal material showing smectic A and C phases did result in only a small increase of the relaxation times and the Cole–Cole distribution parameter. With respect to the confinement effect of aerosil, we can deduce that only thin layers of liquid crystal quite near to the aerosil surface are influenced in their physical behaviour. The main effect of aerosil is the creation of much disturbance in the texture of the liquid crystals.

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