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Molecular alignment of the 4-octyl-4′-cyanobiphenyl liquid crystal filled with SiO_2

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The molecular dynamics and molecular alignment of the dispersed 4-octyl-4′-cyanobiphenyl (8CB) liquid crystal with 5 wt% of SiO_2 nanosphere particles have been studied using dielectric spectroscopy. The measurements were performed in the frequency range between 10^2–10^7 Hz in the SmA, N and I phases. The results show only one Debye relaxation process at high frequency (10^5–10^7 Hz). In the bulk material, activation energies of 40, 58 and 63 kJ mol^{-1} were determined for the SmA, N and the I phases, respectively. In the dispersed sample, the activation energies were found to be 52, 76 and 81 kJ mol^{-1}, respectively. These results are compared with the available data in the literature. The reversible electromechanical response of the dispersed sample under the influence of an applied a.c. electric field was investigated in the SmA, N, and I phases.

1. Introduction

The effect of silica nanosphere particles on the ordering and structural properties of a liquid crystal has been the subject of many investigations [1–14]. These studies are of importance for technological applications, especially in the field of the liquid crystal display (LCD) with memory effect [14–17]. In this respect, dielectric spectroscopy is considered an indispensable tool to extract information on the molecular dynamics and molecular alignment of these liquid crystal materials. Recently, attention has been paid to the relaxation behaviour, molecular dynamics, and phase transition of the *n*CB (cyanobiphenyl) liquid crystals (with $n=5$, 7, and 8) [18–26]. It is known that these materials have chemical structures differing only in the number of methylene groups added to the terminal attached alkyl group (C_nH_{2n+1}). They all show different mesophases with a convenient range of temperature (20–40°C). The dipolar moment of these compounds is due mainly to the terminal cyano group. As an approximation this moment is considered to be along the molecular long axis.

In 1994, Schwalb and Deeg [3] investigated the effect of pore size on the orientational dynamics of a liquid crystal confined in a porous glass. For 8CB, they found a drastic reduction of the relaxation time in comparison with the bulk sample. In 1998, Sinha and Aliev [10] reported the influence of spatial confinement on the dielectric properties of 8CB in its Smectic A (SmA), nematic (N) and isotropic (I) phases. In their experiment a porous glasses with mean pore size 100 and 1000 Å respectively were used as confinement systems. In the frequency range 10^{-2}–10^9 Hz they identified four relaxation processes. In 2004, Ryabov *et al.* [25] studied the temperature dependence of the tumbling mode relaxation time of 8CB confined in a nanoporous matrix. Their results showed non-monotonic behaviour in the temperature region below the N–I transition at $T_{\text{N-I}}=313$ K. At $T>T_{\text{N-I}}$, the tumbling relaxation mode exhibited Arrhenius behaviour. Jin and Kim [26] investigated the behaviour of the real part ε' and imaginary part ε'' of the dielectric constant of bulk 8CB at low frequency range 0.1 Hz–200 kHz.

In our previous work [6], dielectric spectroscopy was used to obtain information on the molecular dynamics and molecular alignment of 5CB nematic liquid crystal, as bulk sample and as samples filled with various concentrations of silica nanoparticles. The dielectric measurements were performed in the frequency range 10^2–10^7 Hz in the N and I phases, where one relaxation process was identified. The effect of an applied electric field on the molecular alignment of the silica-filled 5CB samples in the same frequency range was also studied. The interesting results showed the possibility of obtaining electromechanical switching of these samples in the N phase.

In the present work, we apply our dielectric spectroscopy technique to the study of the molecular dynamics

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and molecular alignment of 8CB liquid crystal as a pure sample and as samples containing 5 wt% of SiO_2 nanoparticles in the SmA, N and I phases. This concentration was chosen to be in the middle of the range for technical applications reported in the literature.

2. Experimental

The experimental arrangement has been described in detail elsewhere [6]. In our experiments samples of 4-octyl-4′-cyanobiphenyl (8CB) obtained from E. Merck (Darmstadt, Germany) are used as obtained. The filler used is a white amorphous hydrophilic silica powder obtained from Degussa - Huels, Germany. It was produced by precipitation from aqueous solution, its solid density is $2.1\,\mathrm{gm\,cm^{-3}}$ and the primary particle size is 30–80 nm as calculated from the specific surface area of $175\,\mathrm{m^2\,g^{-1}}$. The filled samples were prepared by mixing weighed amounts of silica particles and 8CB on a metal plate at room temperature. By stirring with a rod it was easy to obtain the formation of a uniform liquid crystal/silica dispersed sample. We surrounded the sample on a stainless steel circular plate with a circular polyimide spacer of 0.125 mm thickness (inner diameter 19 mm, outer diameter 20 mm), and covered it with another stainless steel circular plate of smaller diameter. The experimental set-up consists of a sample holder, heat chamber, temperature regulator, and a Solartron frequency response analyser (model 1260) connected to a computer. The heating element is connected with a temperature regulator capable of maintaining the temperature within $\pm 0.1^\circ\mathrm{C}$ in the range -190 to $160^\circ\mathrm{C}$. A platinum resistor (Pt100) is used in the regulator to sense the temperature, forming a feed-back loop with the controller. In these experiments, a sample is pre-treated by heating to the isotropic phase at 330 K. It is then cooled gradually to reach the SmA phase at room temperature.

The capacitance and conductance of the sample condenser were measured using over the frequency range 10^2–10^7 Hz; the impedance measurements in this frequency range can be performed step by step. The applied signal amplitude is 0.2 V for all the dynamic measurements. From the measurements of the complex impedance, the analyser evaluates automatically the capacitance and conductance values. A computer collects these values at different frequencies from the analyser and the values of the dielectric permittivity and dielectric absorption are then calculated. The accuracy of the measurements was confirmed by the measurement of a known low loss teflon capacitor inside the chamber. The error in the measurement of the loss tangent is below 1.5% in the region below 1 MHz. Above 1 MHz, the experimental error greatly increased with increasing frequency in the range 1–10 MHz.

The experimental error in the determination of the real part ε' is due mainly to the geometry of the sample condenser (thickness and diameter, including the influence of the spacer). The absolute accuracy for the real part ε' of the dielectric function is estimated to be $\pm 10\%$.

To study the molecular alignment of the samples under consideration, an a.c. electric field at a frequency 50 Hz was applied for 1 min to the sample. At this frequency, the molecular dipoles are able to follow the a.c. electric field, and therefore the domains formed by the silica particles network tend to orient the director of the molecules perpendicular to the plane of the electrodes. The sample was controlled so that the maximum current (at 150 V) was $100\,\mu A$, corresponding to a maximum of 15 mW of dissipated power in the sample; this does not affect the temperature of the sample significantly, since it is placed between stainless steel electrodes. The energy input by the annealing field was then calculated, using the measured conductivity of the sample and the estimated specific heat capacity of the liquid crystal material.

3. Results and discussion

3.1. *Molecular dynamics of the bulk and filled 8CB liquid crystal*

In this experiment, all dielectric measurements of the 8CB liquid crystal as a bulk sample and sample filled with 5 wt% SiO_2 nanoparticles were performed in the frequency range 10^2–10^7 Hz: in the SmA phase (at $T=295$ and 299 K), N phase (at $T=308$ and 311 K) and I phase (at $T=325$ and 329 K). In figures 1 and 2, the values of the real ε' and imaginary ε'' parts, respectively, of the complex dielectric constant ε^* are shown as a function of frequency for the bulk and filled samples in the SmA, N and I phases.

From figure 1, constant values of $\varepsilon'=(8.86\pm0.9)$, (9.67 ± 1.0) and (8.09 ± 0.8) were measured in the frequency range 10^2–10^5 Hz in SmA at $T=295$ K, N phase at $T=311$ K and I phase at $T=325$ K, respectively. These values exceed by 28, 21 and 12% the corresponding values of the filled sample except for $\leqslant 500$ Hz in the I phase. This effect is attributed to the non – perfect orientation of the molecules in the filled 8CB sample that arises from the presence of SiO_2 nanoparticles. From figure 1, it can be seen that between 1 and 100 kHz, the value of ε' reflects the dipole orientation in the sample; at lower frequencies there might be an additional influence of the Maxwell–Wagner polariaztion [26].

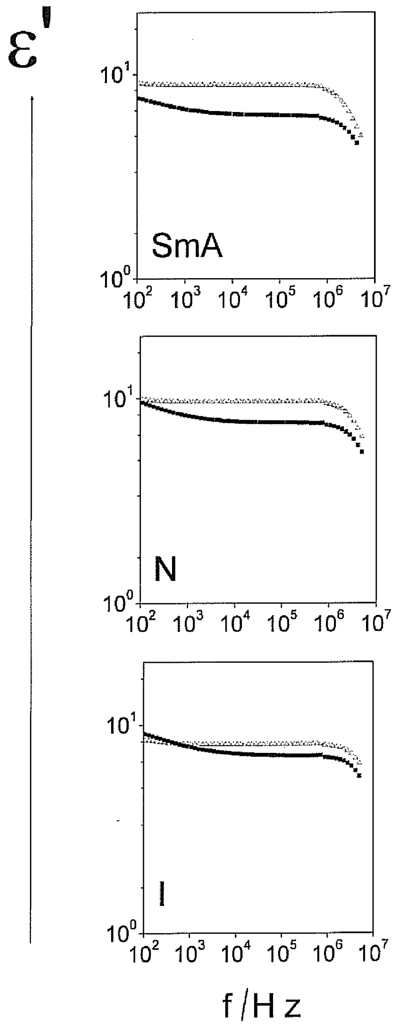

Figure 1. The real part ε' of the complex dielectric permittivity in the frequency range 10^2–10^7 Hz for 8CB liquid crystal as a bulk sample (-△-) and as a sample containing 5 wt% silica particles (-■-) in: the Sm A phase at $T=295$ K, N phase at $T=311$ K, I phases at $T=325$ K.

Figure 2 shows that the imaginary ε'' part of the complex permittivity ε^* of the bulk and filled samples exhibits a one Debye relaxation process in both samples in the frequency range 10^5–10^7 Hz for the SmA, N and I phases. This relaxation is attributed to the rotation of the liquid crystal molecules around their short axis. A similar observation is reported in [10]. From these results, it is noted that as the temperature increases (from the SmA toward the I phase) the relaxation peak frequency f_R is shifted towards higher frequency for both the bulk and filled 8CB liquid crystal samples.

The dynamic behaviour of the liquid crystal may be described by the Cole – Cole relaxation function given by [27]:

$$\varepsilon^* - \varepsilon_\infty = \Delta\varepsilon \Big/ \left[1 + (\iota\omega\tau)^{1-\alpha}\right]$$

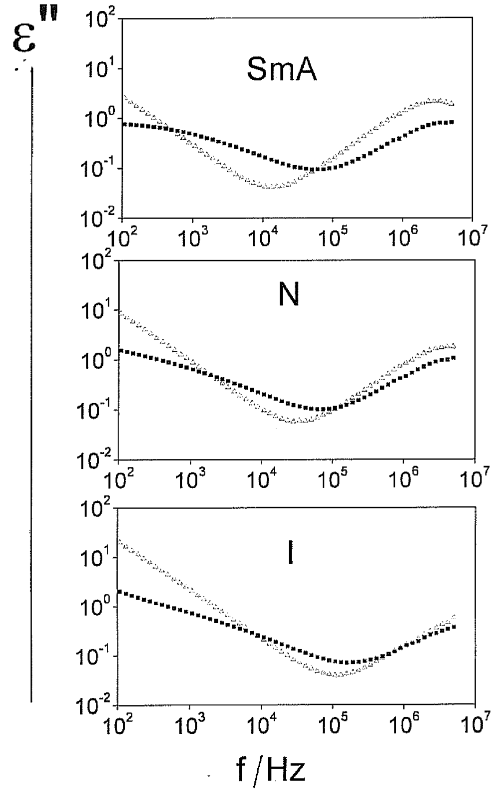

Figure 2. The imaginary part ε'' of the complex dielectric permittivity in the frequency range 10^2–10^7 Hz for 8CB liquid crystal as a bulk sample (-△-) and as a sample containing 5 wt% silica particles (-■-) in: the SmA phase at $T=295$ K, N phase at $T=311$ K, I phase at $T=325$ K.

where ω is the characteristic angular frequency, $\tau = 1/2\pi f_R$ and ε_∞ describes the high frequency limiting value of the real part ε'; $\Delta\varepsilon$ is the dielectric strength, and α is a fractional form parameter ($\alpha<1$) describing the deviation of this relaxation from ideal Debye behaviour. In figures 3 and 4 the value of ε' versus dielectric loss ε'' for both samples under consideration in the SmA phase (at $T=295$ and 299 K), the N phase (at $T=311$ and 308 K) and the I – phase (at $T=325$ and 329 K) are shown in the form of Cole – Cole plots. From these plots the values of the relaxation time τ, the shape parameter α, and the dielectric strength $\Delta\varepsilon$ are extracted and collected in table 1.

From the Debye formalism the activation energy E_a was calculated using the Arrhenius equation given by [27]:

$$\tau = \tau_o \exp(E_a/RT)$$

where τ_o is the relaxation time at high temperature, and R is a constant. The activation energies for all phases of the bulk and filled samples are also given in table 1.

From table 1, for the bulk sample, the shape parameter α in the SmA phase has values of 0.16 and

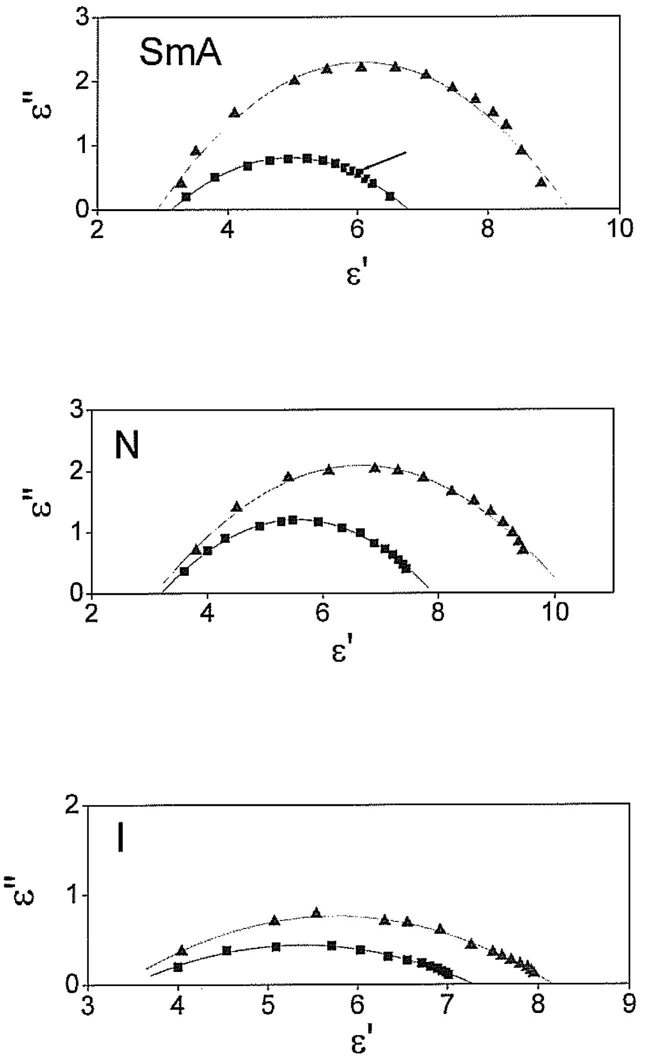

Figure 3. Cole–Cole plot for the bulk (-▲-) and filled (-■) samples (the solid line is a guid to the eye) in: the SmA phase at T=295 K, N phase at T=311 K, I phase at T=325 K.

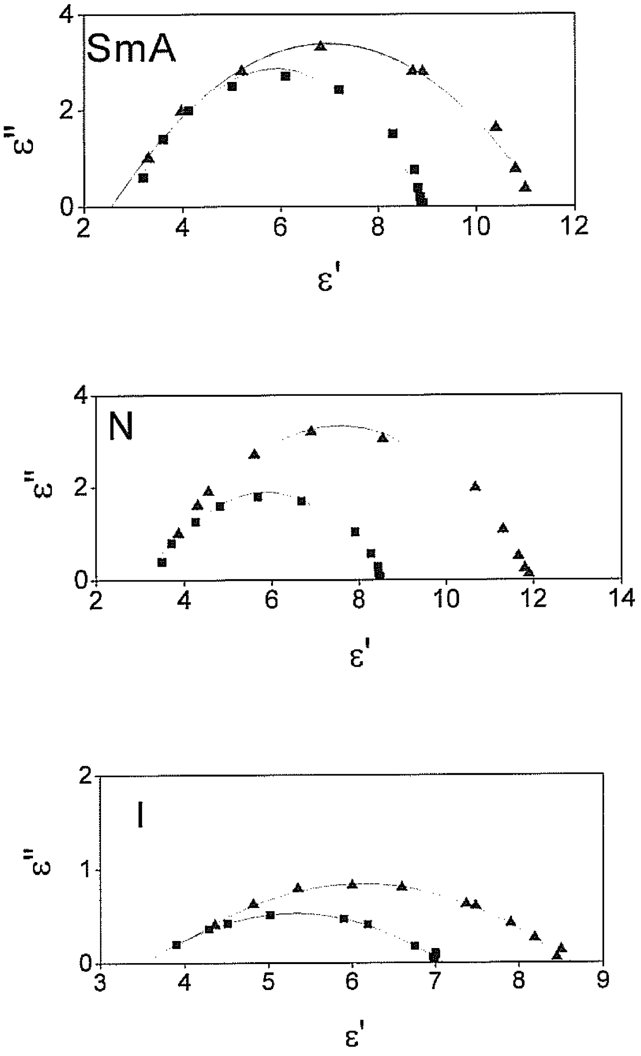

Figure 4. Cole–Cole plot for the bulk (-▲-) and filled (-■-) samples (the solid line is a guid to the eye) in: the SmA phase at T=299 K, N phase at T=308 K, I phase at T=329 K.

Table 1. Shape parameter α, dielectric strength $\Delta\varepsilon$, relaxation time τ, and activation energy E_a for 8CB liquid crystal as a bulk sample and as a sample containing 5 wt% of silica nanoparticles.

Sample	Phase	T/K	α	$\Delta\varepsilon$	$\Delta\varepsilon$ (other work)	τ X 10^{-8} s	E_a/kJ mol^{-1}	E_a/kJ mol^{-1} (other work)
Bulk 8CB	Sm A	295	0.16	5.9	6.1[b]	7.58	40	44.2[a], 43[b]
		299	0.20	8.3	11.0[b]	6.86		
	N	308	0.22	8.5	9.1[b]	4.50	58	58.5[a], 59.8[b]
		311	0.28	6.6	8.9[b]	3.90		
	I	325	0.57	4.6	4.2[b]	1.06	63	28.8[a], 40.8[b]
		329	0.48	4.9	4.4[b]	0.79		
8CB+5 wt% SiO_2	Sm A	295	0.28	3.5	—	7.96	52	50.9[a]
		299	0.13	6	—	6.86		
	N	308	0.25	5.4	—	5.30	76	71[a]
		311	0.27	4.4	—	4.10		
	I	325	0.67	3.6	—	1.60	81	48[a]
		329	0.64	3.4	—	1.32		

[a] Data obtained from [10].
[b] Data obtained from [24].

0.2 at T=295 and 299 K, respectively. These values are less than those obtained in the N phase (at T=308 and 311 K) and the I phase (at T=325 and 329 K). The values of $\Delta\varepsilon$ and E_a extracted for the different phases in the bulk and filled samples may be compared with the corresponding values previously reported [10, 24]. Values of 40, 58 and 63 kJ mol^{-1} are obtained for the bulk sample in the SmA, N and I phases, respectively; in comparison with values of 52, 71 and 81 kJ mol^{-1} for the filled sample. It is clear that a large discrepancy in the activation energy is seen in the I phase in both bulk and filled samples. This may be attributed to a large experimental error because in the I phase the relaxation process occurs near the limit of our frequency range. In the SmA phase in both samples, the activation energy is lower than the corresponding values obtained in the N, and I phases, as reported previously [24]. On the other hand, the activation energy in the SmA, N and I phases in the filled sample is greater than in the bulk. This may be due to the additional potential imposed by the particle surface on the molecules.

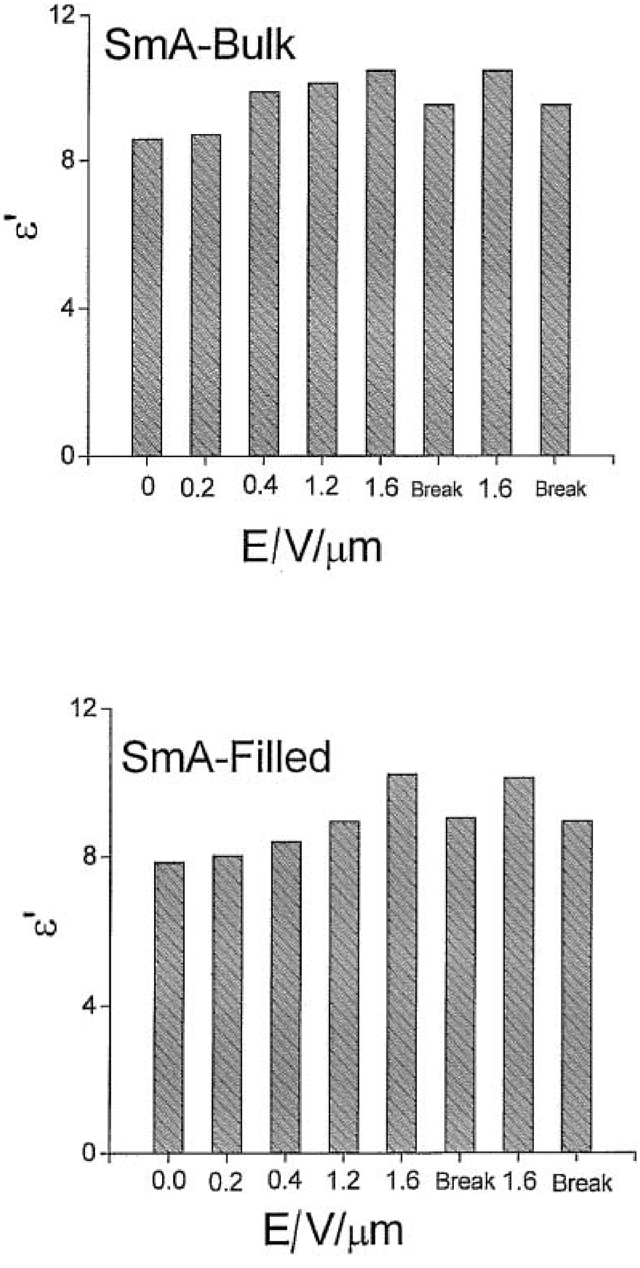

Figure 5. Values of ε' at 10^5 Hz under the influence of an applied electric field for bulk and filled samples in the SmA phase at T=295 K.

3.2. *Molecular alignment of the bulk and filled 8CB liquid crystal*

The effect of application of an electric field on the molecular alignment of 8CB as a bulk sample and as a sample filled with 5 wt% of silica nanoparticles was studied. Homeotropic alignment of the molecules, as a result of the applied electric field, occurred due to a slight charge separation on the molecule, inducing a dipole moment. The electric field causes a reorientation of liquid crystal molecules along the field direction.

The real part of the dielectric constant ε'_s of these samples was measured at a frequency of 10^5 Hz before the relaxation occurred (see figure 1), and was used as a probe to study the influence of the molecular alignment in both the SmA and N phases. In this experiment, ε'_s was measured before applying the external electric field in the SmA phase at T=295 K. Subsequently, an alternating electric field of strength 0.2–1.6 V μm^{-1} with frequency of 50 Hz was used. The advantage of the a.c. electric field is that no chemical reactions at the electrode take place. Nevertheless the dipole moment of the molecules can follow the direction of the applied field, since the relaxation frequency is greater than the frequency of the applied electric field. After 1 min, the applied field was switched off and the value of ε'_s remeasured. The results are presented in the histograms in figure 5 for the SmA phase of the 8CB liquid crystal bulk sample and a sample filled with 5 wt% of silica. From figure 5 it can be seen that the molecular alignment of the bulk sample is slightly influenced by the applied a.c. electric field.

This experiment was repeated in the N phase at T=311 K; the results are shown in figure 6. It is clear that the homeotropic alignment of the molecules in the N phase is more pronounced than in the SmA phase. In this case, after the application of an electric field of strength 0.2 V μm^{-1}, homeotropic alignment of the molecules was established, while a higher electric field strength of 1.6 V μm^{-1} was needed in the SmA phase to achieve the proper alignment, a result of the high

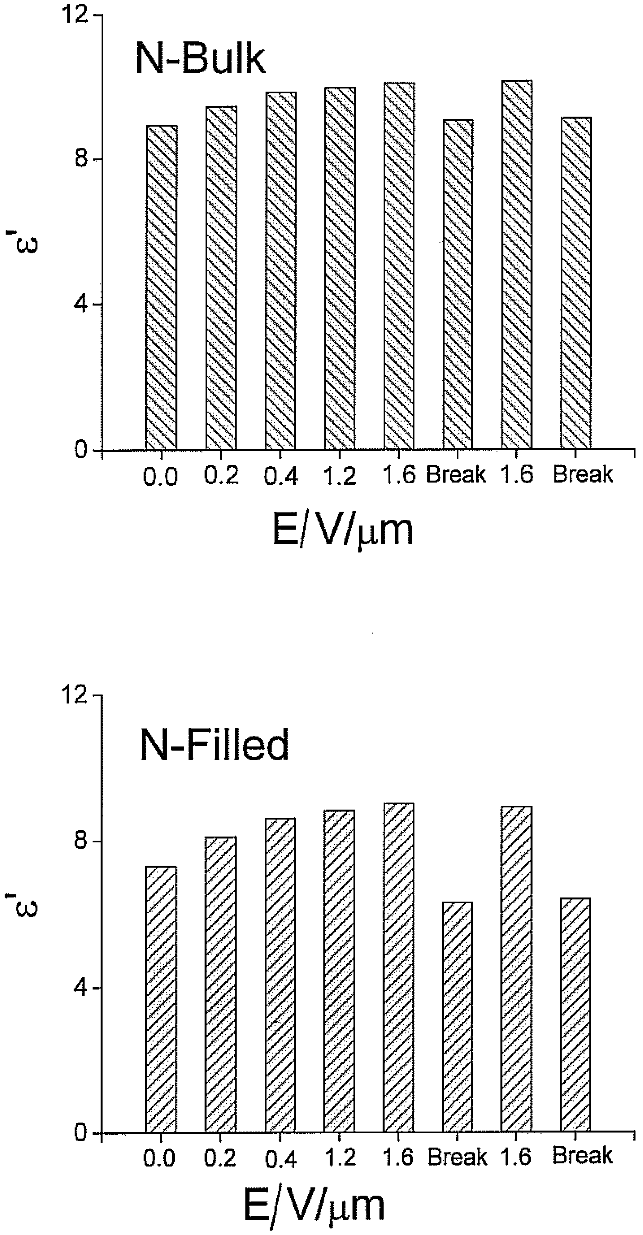

Figure 6. Values of ε' at 10^5 Hz under the influence of an applied electric field for bulk and filled samples in the N phase at T=311 K.

viscosity in the SmA phase. In both phases the value of ε' reached a saturation with no further increase at high field strength of value 1.6 V μm^{-1}. In order to obtain better molecular alignment, the sample was cooled gradually at 0.5 K min^{-1}, while an electric field of strength 1.6 V μm^{-1} was applied. After reaching room temperature at T=295 K, the field was removed and ε' was remeasured in the same phases as discussed above.

In considering the technical applications of this effect, we found that by a small displacement of the stainless steel electrode the alignment of the molecules is destroyed in both phases. For this experiment the position of the upper electrode was shifted slightly back and forth. We found that it does not matter how much and how often this displacement was applied. Thus it is sufficient to change the arrangement of the filler particles inside the liquid crystal matrix to destroy the alignment. At this point we may state that the molecular alignment of the bulk samples is controlled by the metal surface of the electrode, whereas for the filled sample the molecular alignment is controlled by the surface of the filler particles. A similar effect was found in our previous studies of the molecular alignment of 5CB nematic liquid crystal [6].

4. Conclusion

In this report the molecular dynamics and molecular alignment of 8CB liquid crystal, as a bulk sample and as a sample containing 5 wt% of silica, have been studied, using dielectric spectroscopy in the frequency range 10^2–10^7 Hz. The results showed one Debye relaxation frequency in the range 10^5–10^7 Hz. We found that to achieve molecular alignment, a higher a.c. electric field strength was needed in the SmA phase in comparison with the N phase for the filled sample.

The possibility of an electromechanical switch in both SmA and N phases has been studied.

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