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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Bormuth, F. J. , Biradar, A. M. , Quotschalla, U. and Haase, W.(1989) 'Influence of spacer length on dielectric properties of polymeric liquid crystals', *Liquid Crystals*, 5: 5, 1549 – 1557

To link to this Article: DOI: 10.1080/02678298908027790

URL: <http://dx.doi.org/10.1080/02678298908027790>

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Influence of spacer length on dielectric properties of polymeric liquid crystals

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For a liquid-crystalline side chain polymer with cyanobiphenyl mesogenic groups and a spacer length of four methylene groups the dielectric properties over a wide frequency range are studied. They are compared with a previously published analogous compound with six spacer groups in order to get the spacer length dependence of dielectric relaxations. Both compounds have been analysed in terms of theoretical relaxation curves. The δ -relaxation is more asymmetrically broadened and shifted to longer relaxation times for shorter spacer. This is consistent with its molecular interpretation as end-to-end rotation around the short molecular axis. The relaxation in perpendicular orientation is strongly shifted to longer relaxation times and shows another temperature dependence for shorter spacer. This behaviour is attributed to superposition of up to three separate relaxation processes.

1. Introduction

The molecular dynamics of liquid-crystalline side chain polymers with help of dielectric relaxation spectroscopy has been the subject of continuous interest since the first reports by Kresse and Talrosé [1] and Zentel *et al.* [2]. A series of works, especially on oriented samples [3-8], revealed that two main relaxation processes with rather different characteristics exist.

The low frequency δ -relaxation was found exclusively in homeotropic ($\mathbf{n} \parallel \mathbf{E}$) and incomplete orientation. It is attributed to end-to-end reorientation of the side chains, much like the low frequency process in low molecular weight liquid crystals [9], though more cooperative.

The high frequency relaxation (or α -relaxation, but this expression is also used for amorphous polymers) is mostly described as a superposition of different molecular processes. In a recent work [10] we proposed to separate this relaxation into two subprocesses.

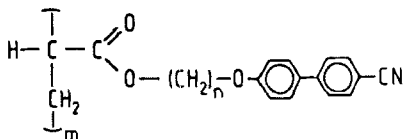
The study of the spacer length dependence of these dielectric phenomena is interesting mainly for two reasons:

being an end-to-end reorientation, the properties of the δ -relaxation should be very sensitive to spacer length; and
the different terms in the α -relaxation might have different spacer length dependence, leading to changes in the overall properties of the composed process.

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2. Experimental

The principal structure of the substances is shown below.



Compound	<i>n</i>	Phase sequence (<i>T</i> in °C)	Molecular weight
1	4	g 30 N 102 I	~ 6000
2	6	g 32 N _r 54 S _A 95 111 I	6000

Both compounds with $n = 4$ and $n = 6$ were synthesized by our group. The synthesis of the monomers started from the corresponding cyano-hydroxo-biphenyls, which were kindly supplied by E. Merck Co., Darmstadt, F.R. Germany.

The syntheses were done using standard methods described elsewhere [11]. The monomer was purified chromatographically using a silica gel-methylene chloride column. Afterwards it was dried for several days in a dry chamber at about 100°C to remove the solvent. The polymerization was carried out in DMF at 70°C, using AIBN (1 mol %) as initiator. The purification of the polymer was done by preparative gas phase chromatography.

The transition temperatures and phase sequences as given above were determined by polarization microscopy, differential scanning calorimetry (D.S.C.) and X-ray diffraction of oriented samples. The occurrence of smectic and reentrant nematic phase in **2** has already been reported [12]; compound **1** shows only typical nematic X-ray diagrams.

Dielectric measurements were performed in a frequency range of 10^{-1} – 10^7 Hz. For **2** this means an extension of the previously published measurements [4] to lower frequencies. The different devices used for this frequency range have been described elsewhere [4–6].

3. Results and discussion

X-ray diagrams were taken for samples oriented by a magnetic field. For **1** a typical nematic pattern was found with a wide angle reflection corresponding to an intermolecular distance of 5.0 ± 0.1 Å. The small-angle reflection is very weak and yields an average molecular length of 40 ± 10 Å. For **2** the X-ray pattern was identical in the nematic phase. In the smectic phase a layer distance of 34 ± 1 Å was determined. Both values are larger than the theoretical length of the monomer units, which is estimated as 20 Å for **1** and 22 Å for **2**. This means that a considerable overlap of the side groups exists in the two compounds.

In the temperature dependent plot of ϵ' for **1** (see figure 1) we find one step in homogenous orientation ($\mathbf{n} \perp \mathbf{E}$) just above the glass transition temperature and one step in homeotropic orientation at $T \approx 60^\circ\text{C}$. An analogous behaviour was also found for **2** [4]. The relaxation process corresponding to the step in homogeneous orientation will be referred to as \perp -relaxation, and the step in homeotropic orientation is assigned to the well known δ -relaxation. The frequency dependences of both relaxations are plotted in figures 2 and 3 for different temperatures.

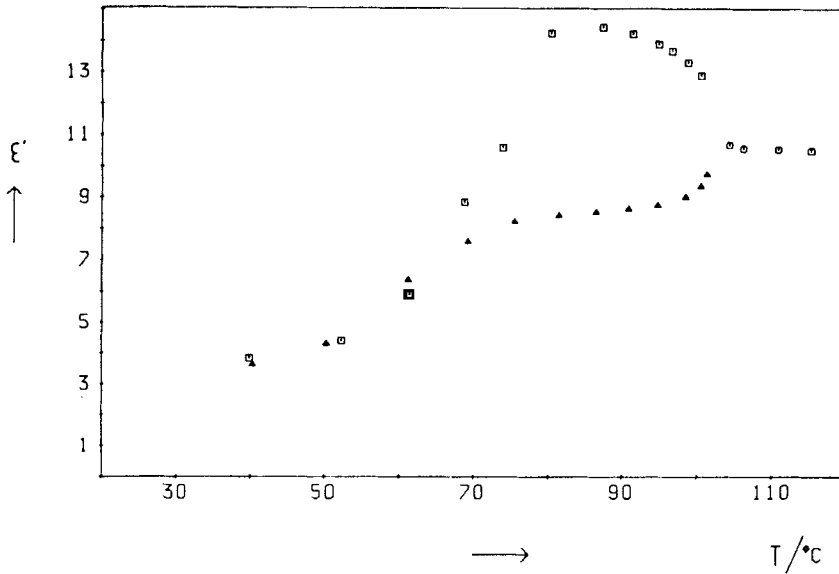


Figure 1. Real part of dielectric permittivity versus temperature for 1 at $f = 0.11$ kHz. (\square) \parallel -orientation, (\blacktriangle) \perp -orientation, (\circ) isotropic.

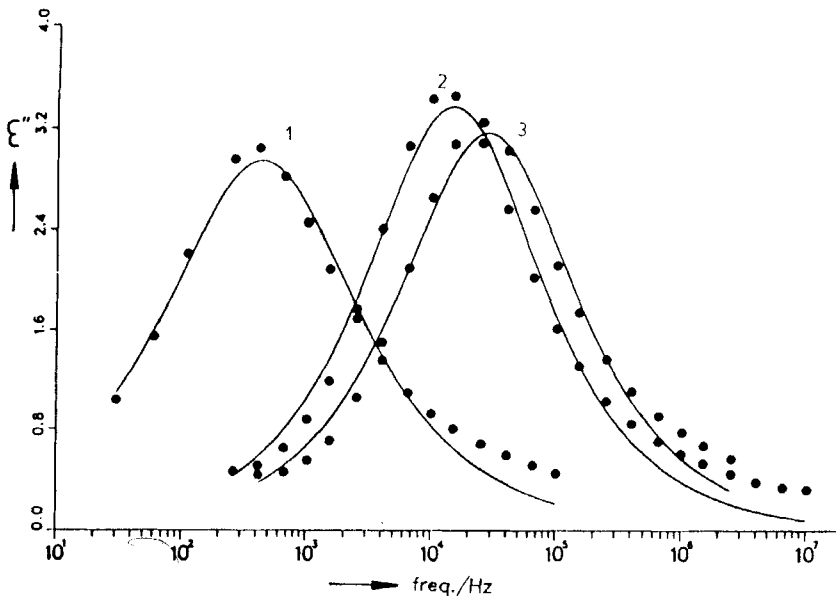


Figure 2. ϵ'' versus frequency in \parallel -alignment for 1; solid lines are fitted curves using equation (1) with $n = 1$. Experimental errors are within point size. Curve 1, $T = 73.8^\circ\text{C}$; curve 2, $T = 94.6^\circ\text{C}$; curve 3, $T = 98.6^\circ\text{C}$.

The imaginary parts of the dielectric permittivity $\epsilon''(\omega)$ have been approximated numerically by a superposition of Fuoss-Kirkwood (F.K.) functions of the form

$$\epsilon''(\omega) = \sum_{i=1}^n \left(\frac{\epsilon_{m,i}}{\cosh[\beta \ln(\omega/\omega_{0,i})]} \right), \quad (1)$$

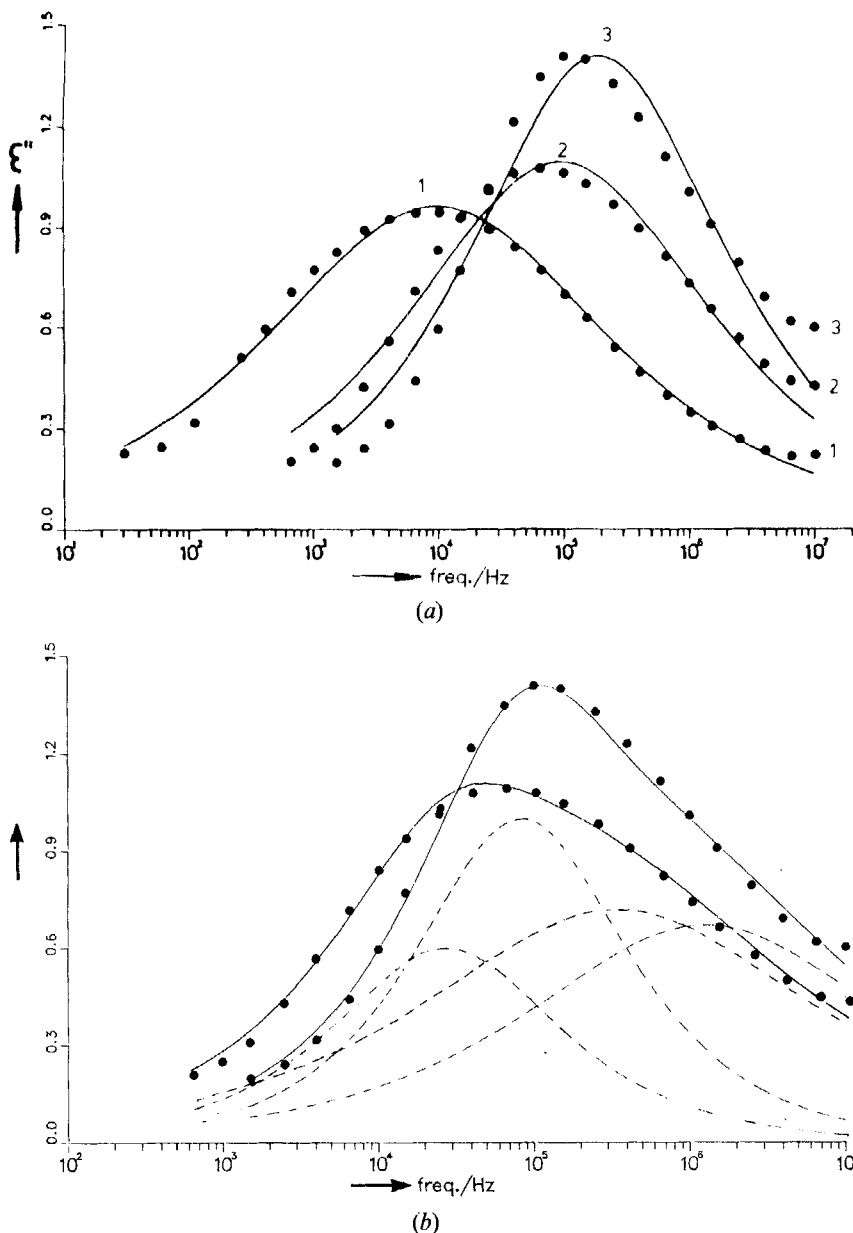


Figure 3. ϵ'' versus frequency for \perp -orientation and fitted curves (solid lines) according to equation (2) for 1. Experimental errors are within point size. (a) One-line fit ($n = 1$): Curve 1, $T = 75.4^\circ\text{C}$; curve 2, $T = 90.8^\circ\text{C}$; curve 3, $T = 100.4^\circ\text{C}$. (b) Two-line fit ($n = 2$): curve 1, $T = 100.4^\circ\text{C}$; curve 2, $T = 90.8^\circ\text{C}$.

where ϵ_m is the maximum value of ϵ'' , ω_0 is 2π times the relaxation frequency and β is the F.K. distribution parameter.

For the δ -relaxation a description by one F.K. function is appropriate except for small deviations at higher frequencies (see figure 2). These deviations can be described by a superposition of a second, broad F.K. curve; however, the fit parameters of this second curve show rather poor reproducibility. Therefore we tried

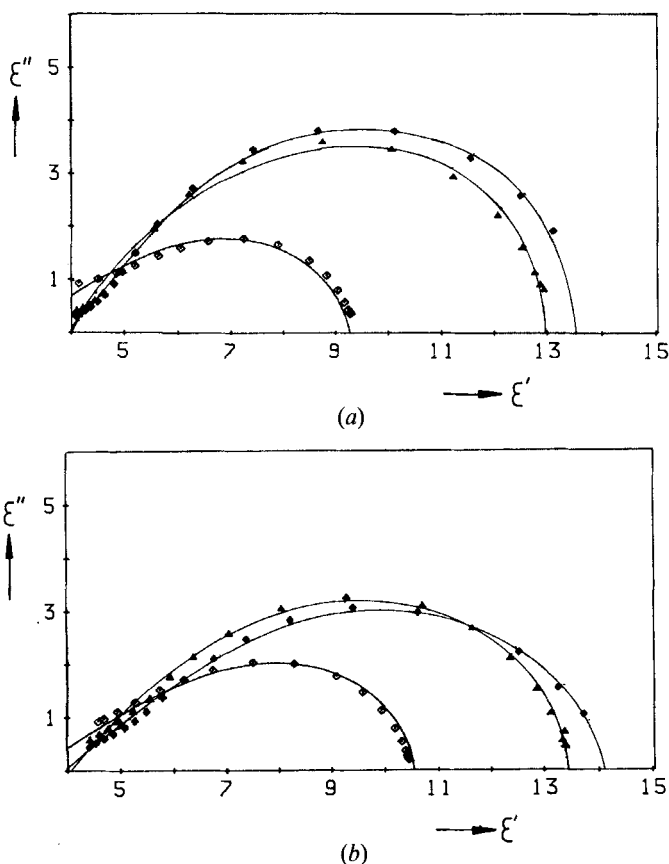


Figure 4. Cole-Cole plots for δ -relaxation. Experimental errors are within point size. (a) Compound 1: (Δ) $T = 98.6^\circ\text{C}$, (\blacklozenge) $T = 73.8^\circ\text{C}$, (\diamond) $T = 115.2^\circ\text{C}$. (b) Compound 2: (Δ) $T = 92.9^\circ\text{C}$, (\blacklozenge) $T = 72.6^\circ\text{C}$, (\diamond) $T = 114.0^\circ\text{C}$. The solid lines are fitted curves according to equation (3).

to approximate the δ -relaxation also by using the asymmetric Havriliak-Negami (H.N.) function

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[(1 + i\omega/\omega_0)1 - \alpha]^\beta} \quad (2)$$

In the H.N. function β describes the asymmetry of the curve and α is a measure of its width.

Both the real and the imaginary parts of the complex permittivity were fitted by H.N. We obtained rather a good approximation, especially for ε' (see figure 4), and very reproducible parameters, which are given in table 1, together with the F.K. distribution parameters for one-line fits.

We now discuss the differences of the relaxation parameters between the two compounds. Generally, for the compound with shorter spacer, 1, the tendency is a decrease of β for the F.K. approximation (broadening) and a decrease of β with unchanged α for the H.N. approximation (more asymmetry). The increase of asymmetry for 1 is obvious in the complex-plane plots (see figure 4). Relaxation strengths are somewhat larger for compound 2. This may be explained by a stronger antiparallel

Table 1. Fit parameters for Havriliak–Negami (H.N.) approximation and Fuoss–Kirkwood (F.K.) distribution parameter β for comparison; f_r , logarithm of relaxation frequency in Hz; α (H.N.), β (H.N.), $\epsilon_0 - \epsilon_\infty$ (H.N.), ϵ_∞ (H.N.), parameters of equation (2); for H.N. fit, average values of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are given. The last column is the average deviation per point between experimental and calculated values.

Compound	$T/^\circ\text{C}$	f_r (H.N.)	α (H.N.)	β (H.N.)	$\epsilon_0 - \epsilon_\infty$ (H.N.)	ϵ_∞ (H.N.)	β (F.K.)	$d(x_i)$
1	115.2	149	0.08	0.41	7.1	3.43	—	0.007
	100.4	17.9	0.07	0.53	8.9	3.93	0.64	0.010
	94.6	7.3	0.06	0.57	9.9	4.05	0.68	0.011
	91.2	3.9	0.06	0.58	10.3	4.02	0.69	0.012
	80.2	0.79	0.06	0.58	10.9	3.99	0.75	0.017
	73.8	0.146	0.08	0.48	10.2	3.83	0.62	0.017
	68.8	0.062	0.05	0.48	10.1	4.07	0.56	0.012
2	114.0	227	0.12	0.47	6.1	3.34	0.56	0.005
	108.4	63.0	0.03	0.58	7.7	3.71	0.67	0.009
	101.3	24.8	0.0	0.62	8.5	3.71	0.73	0.005
	92.9	8.3	0.0	0.60	9.1	3.95	0.75	0.006
	86.0	4.0	0.05	0.68	9.3	3.91	0.75	0.007
	79.2	1.5	0.02	0.64	9.5	3.91	0.75	0.006
	72.6	0.52	0.0	0.60	9.5	3.86	0.75	0.006
	66.8	0.21	0.0	0.59	9.5	3.83	0.69	0.007

molecular association in compound **2**, due to the smectic phase. Indeed, in the low temperature nematic phase of **2** the relaxation strength tends to increase [4].

In the Arrhenius plot (see figure 5) the δ -relaxation shows linear behaviour at higher temperatures. The activation energy determined is significantly larger for **1** than for **2**. This is also true for the isotropic phase. At lower temperatures both compounds tend to deviate from the Arrhenius behaviour.

The \perp -relaxation was approximated by either a single or a superposition of two F.K. functions (see figure 3). Single-line approximation gives a broad relaxation time distribution (small β values). β is of the same order of magnitude for both compounds. It is important to note that β increases as the clearing point is approached (see table 2); this effect is similar for both compounds. In parallel to this is an increase in the maximum value of ϵ'' , while the overall relaxation strength remains nearly constant; this means that we have a narrowing of the relaxation curve with increasing temperature.

The temperature dependence of the relaxation frequencies determined from single-line approximation is shown in figure 5. The plot is non-linear over the whole temperature range, approaching nearly constant values close to the clearing point. The values for the compound with a shorter spacer are about 1 decade smaller than those with a longer spacer.

Two-line approximations always give significantly better agreement with the experimental data, which is reasonable because of the larger number of variable parameters (see table 2). A small, relatively narrow, low frequency curve is added to a broad high frequency curve. For the first curve the relaxation strength shows an increase near the clearing point, whereas for the second it is slightly decreasing. This explains phenomenologically the change in the shape for the composed curve as well as the retardation in the plot of average relaxation frequencies versus the reciprocal temperature (see figure 5) near the clearing point.

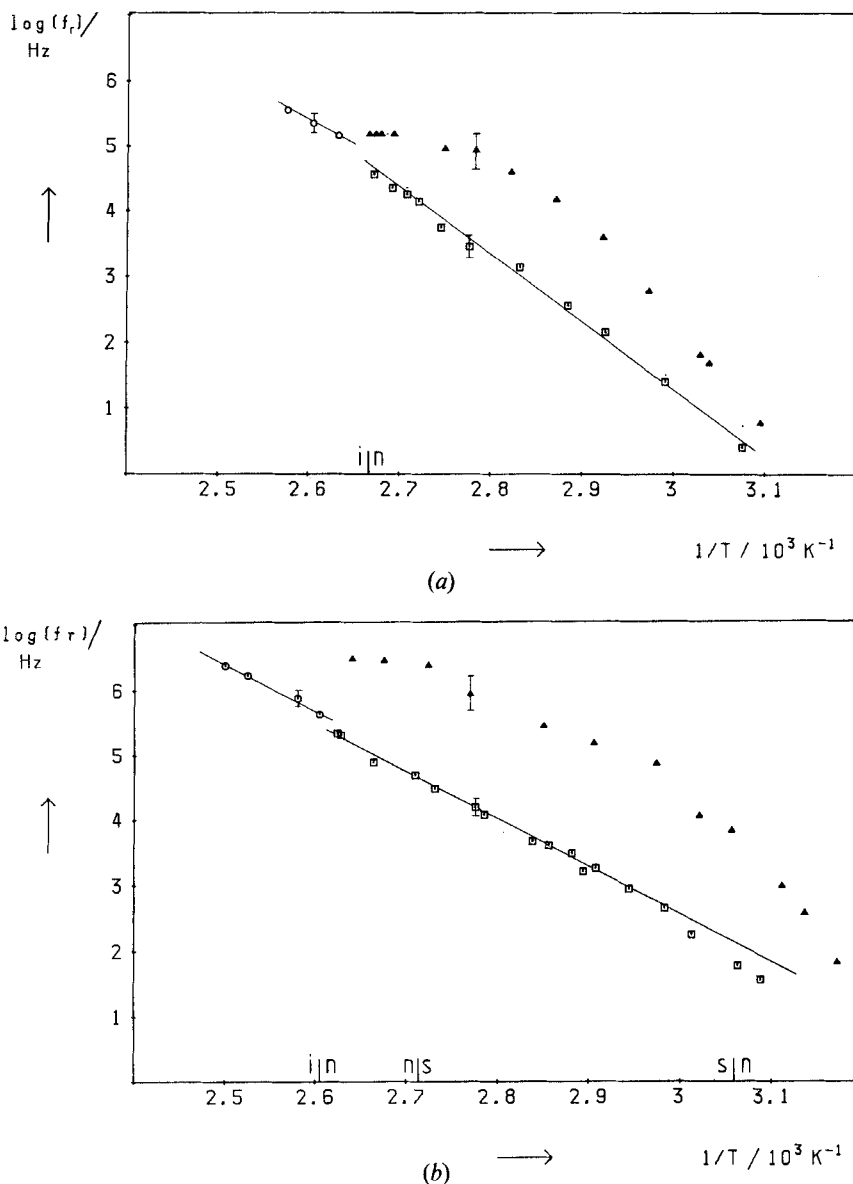


Figure 5. Activation diagrams for (a) compound 1 and (b) compound 2. (\square) \parallel -orientation, (\blacktriangle) \perp -orientation, (\circ) isotropic activation energies in kJ mol^{-1} .

The relaxation curves in the isotropic phase show a very large asymmetric broadening (see figure 4 and table 1). They can be approximated qualitatively by a superposition of two separate relaxations, one with $\beta \approx 0.97$ and $f_r \approx 237 \text{ kHz}$ for **1** ($\beta \approx 0.90$, $f_r \approx 360 \text{ kHz}$ for **2**) and one with $\beta \approx 0.50$, $f_r \approx 1600 \text{ kHz}$ for **1** ($\beta \approx 0.41$, $f_r \approx 3200 \text{ kHz}$ for **2**). The first is clearly the continuation of the δ -relaxation in the isotropic phase. The second appears as a continuation of the high frequency contribution of the \perp -relaxation. The two-line description does not give any information about the low frequency contribution in the \perp -relaxation.

Table 2. Fit parameters for compounds **1** and **2** in \perp -orientation as approximated by equation (1) with $n = 1$ or 2.

T/K	f_i/kHz	ϵ_m	β_1	$\epsilon_0 - \epsilon_\infty$	f_i/kHz	ϵ_m	β_2	$\epsilon_0 - \epsilon_\infty$	$d(x_i)$
Compound 1									
107.1	260	0.25	1.0	0.46	2100	0.84	0.37	4.5	0.015
100	200	0.19	0.98	0.39	2200	0.72	0.34	4.2	0.012
94.8	140	0.15	0.9	0.33	1400	0.66	0.36	3.7	0.007
90.3	110	0.12	0.95	0.25	920	0.63	0.33	3.8	0.008
107.1	1070	0.97	0.43	4.5	—	—	—	—	0.045
100.0	1000	0.81	0.38	4.3	—	—	—	—	0.041
94.8	720	0.74	0.39	3.8	—	—	—	—	0.031
90.3	540	0.70	0.37	3.8	—	—	—	—	0.029
85.9	340	0.66	0.34	3.9	—	—	—	—	0.026
71.3	39	0.66	0.29	4.6	—	—	—	—	0.020
58.1	3.9	0.66	0.31	4.3	—	—	—	—	0.012
Compound 2									
100.4	84	1.0	0.71	2.8	1260	0.67	0.42	3.2	0.007
94.6	41	0.68	0.69	2.0	500	0.73	0.42	3.5	0.005
90.8	27	0.59	0.67	1.8	330	0.71	0.39	3.6	0.011
81.4	7.7	0.57	0.55	2.1	110	0.59	0.38	3.1	0.012
75.4	1.5	0.25	0.64	0.8	17	0.82	0.36	4.6	0.008
100.4	191	1.4	0.47	6.0	—	—	—	—	0.11
94.6	132	1.18	0.43	5.5	—	—	—	—	0.059
90.8	95	1.10	0.40	5.5	—	—	—	—	0.064
81.4	27	1.00	0.37	5.4	—	—	—	—	0.040
75.4	9.1	0.97	0.35	5.5	—	—	—	—	0.023
69	1.8	0.95	0.33	5.8	—	—	—	—	0.006

The anisotropic permittivity can in principle be described by the Nordio-Segrè-Rigatti model [13] with an additional factor A_h [10] which accounts for the main chain dipoles:

$$\epsilon(\omega) - \epsilon = F^2 \frac{4\pi N}{3kT} [\mu_i^2(1 + 2S)A_{00}(\omega) + \mu_i^2(1 - S)A_{01}(\omega)] + G\mu_h^2 f(S)A_h(\omega), \quad (3a)$$

$$\epsilon(\omega) - \epsilon = F^2 \frac{4\pi N}{3kT} [\mu_i^2(1 - S)A_{10}(\omega) + \mu_i^2(1 + \frac{1}{2}S)A_{11}(\omega)] + G\mu_h^2 f(S)A_h(\omega). \quad (3b)$$

Here F is the local field factor, N is the density, $\mu_{i,h}$ are the dipole components, S is the order parameter and $A(\omega)$ are the frequency dependent relaxation functions. The third term with A_h will depend only slightly on the nematic order parameter S , since it has been shown that the main chains have only weak orientational order.

The δ -relaxation must clearly be related to the term A_{00} in equation (3a), which means that it is due to 180° reorientations of the whole mesogenic side group. This is indicated by its dominant appearance in homeotropic orientation and its complete absence in the homogeneous spectrum, its large relaxation strength being comparable with the low frequency relaxation in low molecular liquid crystals [9], the decrease of relaxation strength near to the clearing point according to the S -dependence of A_{00} and the decrease of activation energy above the clearing point, which means that the nematic potential is to be overcome by the motion.

However, differences in the behaviour of low molecular weight liquid crystals manifest themselves in the relatively broad and asymmetric relaxation time distribution (where the asymmetry increases on shortening of the spacer length) and in some deviations from linearity in the Arrhenius plot (see figure 5). This behaviour is related to cooperative relaxation processes in amorphous polymers above the glass transition temperature. A molecular interpretation must take into account the fixing of the side groups to the main chain and the correlation between the orientation of adjacent side groups along the chain. No detailed molecular model for such motions yet exists for liquid-crystalline side chain polymers. In a forthcoming publication [15] we will try to develop a simple model derived from theories on amorphous polymers.

The \perp -relaxation could best be approximated by a superposition of two sub-relaxations. This is reasonable looking at equation (3b), from which there may be three molecular contributions to the \perp -relaxation. However, since the reproducibility of the parameters for the sub-relaxations is not sufficient to make quantitative statements, we will not extend the discussion on the origin of these contributions. Anyway we claim that our analysis shows that the \perp -relaxation can in principle be separated in subprocesses related to the terms in equation (3b). Their separation as well as their relative strength depend on the molecular and dipolar structure and on temperature. The properties of the overall \perp -relaxation, especially its shape and frequency-temperature loci, are determined by the different composition of the sub-relaxations. In this scheme the reduction of the relaxation frequencies for the compound with a shorter spacer is explained by a stronger contribution from the low frequency part of the relaxation. For a more detailed molecular characterization we refer the reader to [14], where the two sub-relaxations could be separated more quantitatively.

This work was supported by the Deutsche Forschungsgemeinschaft. We thank E. Merck Co., Darmstadt, for supplying substances for the preparation. One of us (A.M.B.) wishes to thank the DAAD for financial support.

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