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Comparative investigations of linear and cyclic siloxanes with a swallow-tailed liquid crystal as side chain

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Molecular 'zip-fasteners' consisting of short linear and cyclic siloxane backbones and the same swallow-tailed liquid crystal unit as side group were synthesized. The closing and opening mechanism was studied by dielectric measurements. Thereby an abrupt decrease of the static dielectric constant $\varepsilon_{0\|}$ was observed indicating the antiparallel order of the side groups in the 'closed' state. The dielectric relaxation frequencies of the δ- and α-relaxation for the respective oligomers do not depend on the degree of polymerization which could be the result of the high flexibility of the main chain and the relatively low mobility of the liquid crystalline unit.

1. Introduction

Dielectric measurements give information about the dynamics of dipole reorientation and the mutual orientation of molecular dipoles to each other [1]. If now the sample is a liquid crystal, dielectric investigations can be carried out in different directions with respect to the director. In this way the molecular origin of the experimental data can be better understood [2]. On the other hand, the molecular structure can be systematically changed. One possible way to do this is through polymerization. Therefore, comparative studies on cyclic and linear siloxanes with different degree of polymerization were carried out. The main idea behind this paper was to fix a swallow-tailed liquid crystalline side group via a relatively long spacer to siloxane units. It is known that such swallow-tailed liquid crystals show a tendency to give an antiparallel orientation of their molecular long axes [3]. Therefore, it was of interest whether this effect is enhanced in such a way that the molecules form 'two-dimensional' zip-fasteners or whether it is surpressed in oligomeric liquid crystals. Furthermore, the data could be compared with the results on the mesogenic side group precursor itself in order to see the change in the phase transition temperatures [4] and the dielectric relaxation frequencies [5].

2. Synthesis

The synthetic route to the low molar mass mesogen **M** is given in the scheme. The compound **M** was synthesized by conventional methods [6]. A detailed synthesis will be described elsewhere [6], and here we present only a few data for some intermediate products.

4-[4-(hex-5-enyloxy)benzoyloxy]benzoic acid **2**: Cr 136 N 230 is (°C).
Di-*n*-nonyl 4-hydroxybenzylidenemalonate **3**: m.p. 59 (°C).

The overall yield in this synthesis relative to 4-(hex-5-enyloxy)benzoic acid amounted to 26 per cent. The product **M** was recrystallized and purified by column chromatography on silica gel using chloroform as solvent. No additional by-products could be detected by HPLC. Linear (**L**) and cyclic (**C**) siloxane derivatives containing 6–8 (**L6–L8**) and 4–6 (**C4–C6**) $-SiHCH_3-O-$ units, respectively, were obtained from the Consortium für Elektrochemische Industrie GmbH, München. The oligomers were prepared by the classical hydrosilylation reaction [7, 8] between the mesogen and the respective polymethylhydrogensiloxane in the presence of a platinum catalyst. After that, the products were reprecipitated in methanol/chloroform and then purified by column chromatography (Al_2O_3/chloroform) in order to reduce the conductivity. By TLC compound **M** and by IR spectroscopy the Si–H band (2140–2160 cm^{-1}) could not be detected. The samples were characterized by DSC and heated stage, polarizing optical microscopy. As an example, the DSC trace of **L6** is presented in figure 1. The broadening of the phase transition temperatures N/is (half-width about 1·5 K) results mainly from small amounts of homologous polymethylhydrogensiloxanes which could not be separated completely by careful fractionation of the starting material.

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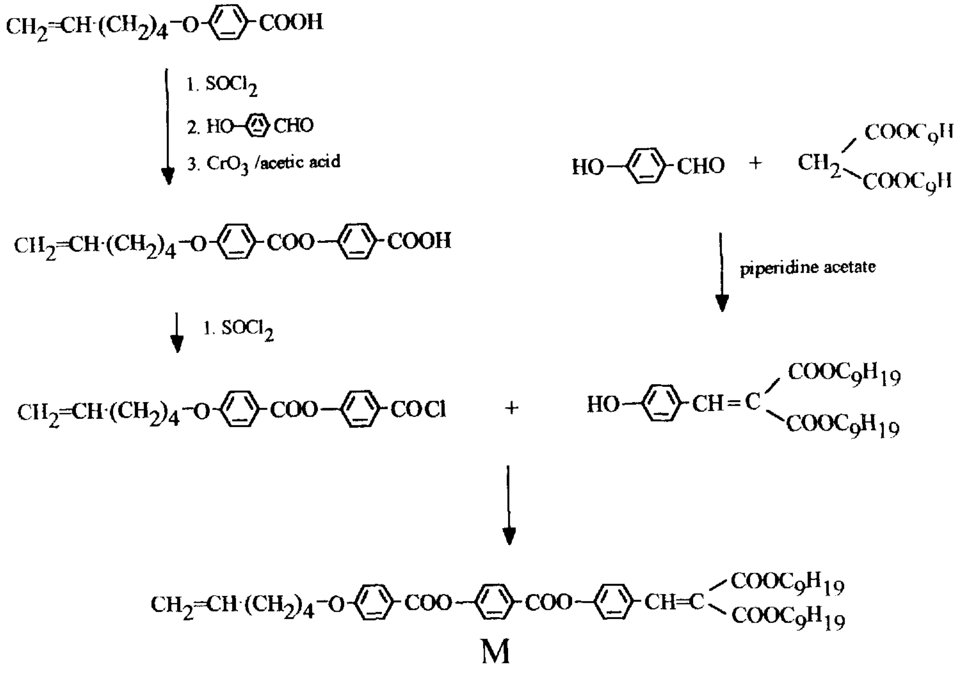
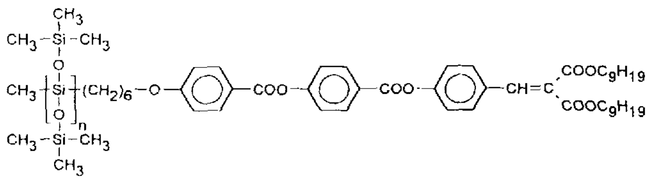
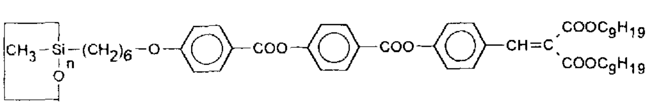


Scheme Synthesis of the swallow-tailed mesogenic moiety (**M**).

The phase transition temperatures and the respective liquid crystalline phases of the linear (**L***n*)



and cyclic (**C***n*)



siloxanes are listed in table 1.

3. Dielectric investigations

Dielectric measurements were carried out in a microcapacitor ($A \approx 1\,\mathrm{cm}^2$, $d = 0{\cdot}2\,\mathrm{mm}$) using a HP 4192A impedance analyser and at low frequencies a Solartron Schlumberger Impedance Analyser SI 1260 together with a Chelsea Dielectric Interface. The samples were oriented in a magnetic field of 0·6 T. In the case of the cyclic siloxanes the orientation obtained was not satisfactory. The temperature was stabilized with a Eurotherm control to ±0·1 K.

The dielectric absorption curves and the Arrhenius plot for the mesogenic side group precursor **M** are given in figures 2 and 3, respectively.

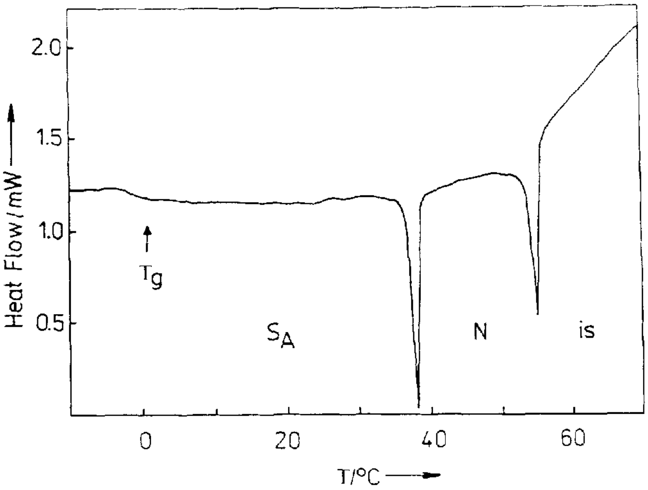


Figure 1. DSC trace of **L6** (10 K min^{-1}, 14·03 mg).

The dielectric loss was fitted to the Cole–Cole equation [1],

$$\varepsilon'' = \mathrm{Im}\left(\varepsilon_\infty + \frac{\Delta}{1 + (\mathrm{i}f/f_\mathrm{R})^{1-h}}\right) \qquad (1)$$

where the dielectric increment Δ, the relaxation frequency f_R and the Cole–Cole distribution parameter h were calculated for both directions. ε_∞ means the high frequency dielectric constant. The conductivity responsible for the increase of ε'' at low frequencies was taken into account by an additional term $A{\cdot}f^{-n}$ ($n > 0$). Within the

Table 1. Phase transition temperatures of the oligomers and the monomer **M**.

Compound	is/N	N/S$_A$	T_g
L6	331	314	269
L7	340	316	269
L8	341	323	—†
C4	350	313	268
C5	348	315	—†
C6	348	314	—†
M	350	313	268(S$_A$/S$_C$)

† The onset temperature of the glass transition could not be detected clearly.

experimental error of $\Delta h_{\|}$ equal to $\pm 0{\cdot}03$, we obtained a classical Debye behaviour with $h_{\|} = 0$. Additionally in figure 1, a dielectric absorption curve in the perpendicular direction is presented. Here also a small absorption maximum (with a maximum of $\varepsilon''_{\perp} \approx 0{\cdot}08$) was detected. Assuming that both processes are related to the same mechanism, one can estimate the degree of the orientation for the domains [9] as $S_d = 0{\cdot}8$ (see equation (3)) from the ratio of the absorption intensities of about 1 : 13.

The Arrhenius plot of $f_{R\|}$ (δ-mechanism) shows a step in f_R at the is–N transition and different activation energies in the liquid crystalline phases. The unexpectedly high value in the nematic state may be the result of pre- and post-transitional effects of the short range nematic order. Due to crystallization of the sample, only a few points for the high frequency absorption (α-process) connected with the reorientation about the molecular long axis could be measured.

The static dielectric behaviour of the mesogenic moiety shown in figure 4 corresponds well with results obtained on other swallow-tailed compounds, i.e. the strong decrease of $\varepsilon_{0\|}$ on cooling. This indicates the tendency to form aggregates of antiparallel oriented molecules due to steric effects [3]. The changing slope of the ε_{0is}/T curve near to the is–N transition can also be considered as suggestive of antiparallel oriented molecules [10].

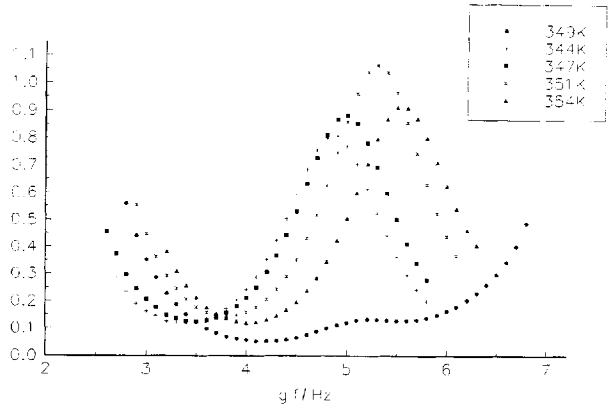


Figure 2. The measured dielectric loss of the swallow-tailed mesogenic moiety in the parallel orientation and the perpendicular direction (only 349 K) at lower frequencies (δ-relaxation). The intensity of the low frequency absorption observed in both directions decreases in the smectic A phase ($T < 350$ K).

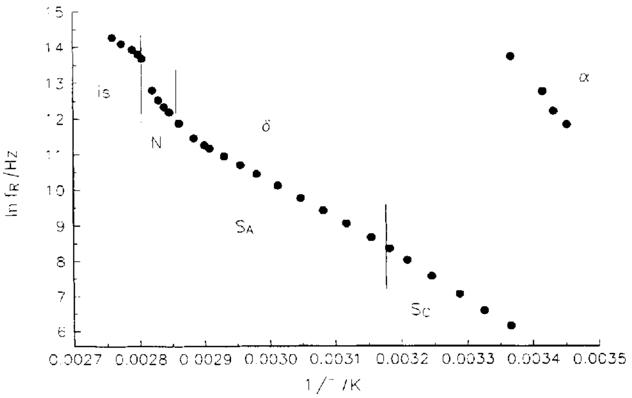


Figure 3. Arrhenius plot of the relaxation frequencies for the mesogenic side group. Phase transitions are indicated. The activation energies E_A/kJ mol^{-1} are 96 (is), 198 (N), 86 (S$_A$) and 100 (S$_C$). Crystallization limited the data points obtained for the high frequency α process.

Generally, the dielectric behaviour of the oligomeric siloxanes is similar to that of mesogen **M**. But, there are some differences which are related to the different chemical structure: (i) the δ-process is observed at lower frequencies where the influence of the conductivity is stronger and (ii) due to the presence of homologous siloxanes, the distribution parameter $h_{\|} > 0$. By way of example, the fit parameters for the ε'' values of the linear oligomer **L6** are given in table 2. Experimental data for **L6** at lower temperatures are presented for both $\varepsilon''_{\|}$ and $\varepsilon''_{\perp}$ on a logarithmic scale in figure 5. From this, the respective value of the degree of director orientation $S_d > 0{\cdot}9$ can be estimated, if one considers deviations of the measured points of ε'' in the perpendicular direction from the fitted curve. The same S_d value was obtained for the other two linear siloxanes.

The static dielectric constant of **L6** shown in figure 6 is much higher than that of the mesogen **M** in figure 4, indicating the influence of the dipoles in the siloxane chain. The decrease in the static dielectric constant in the direction of the preferred axis on cooling is almost abrupt. This general behaviour could also be observed (figure 6) for **L7** and **L8**.

In spite of the repeated purification, the δ-relaxation could not be measured satisfactorily for all samples. The detection of the δ-process was limited by the increasing loss due the conductivity at low frequencies and a decreasing absorption intensity at lower temperatures (see figure 7). Experimental data for **L7** are published

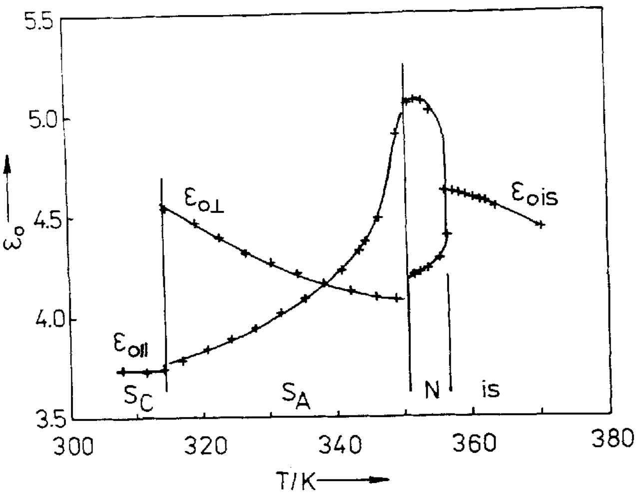


Figure 4. Static dielectric constants of the mesogenic moiety in the different phases.

Table 2. Fit parameters of the measured ε'' values for **L6** to the Cole–Cole equation (δ-relaxation).

T K	is (335 K)	N (327 K)	N (318 K)	S_A (313 K)	S_A (307 K)
$\Delta_\parallel$	2·07	4·03	2·65	2·86	2·26
$f_{R\parallel}$/Hz	14623	1222	279	98·7	23·1
$h_\parallel$	0·78	0·78	0·79	0·73	0·72

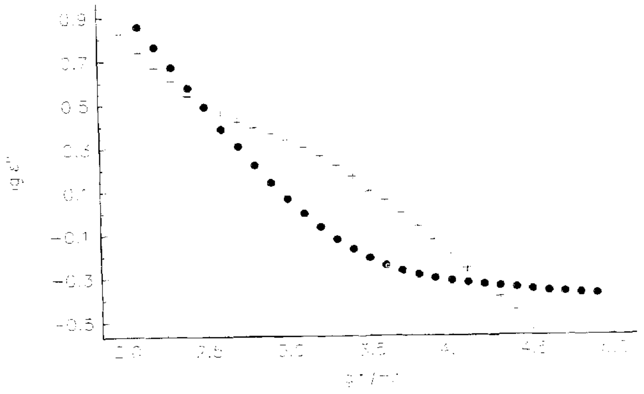


Figure 5. Dielectric absorption ε'' versus the frequency for **L6** at $T = 325$ K (N phase); (+)$\varepsilon''_\parallel$, (●)$\varepsilon''_\perp$. The conductivity part can be seen as a linear function on the double logarithmic scale.

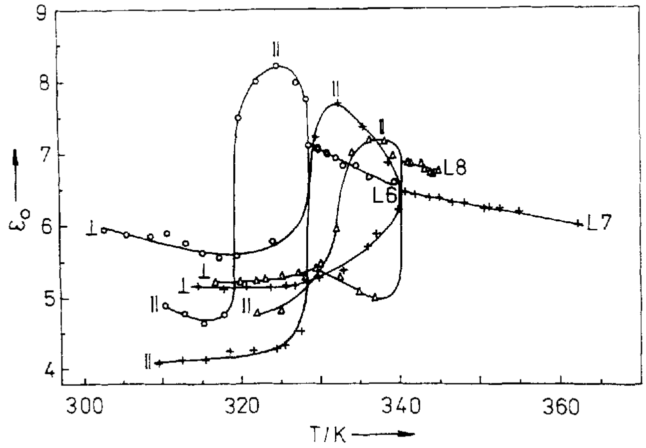


Figure 6 Static dielectric constants of the linear oligomers: (○) **L6**, (+) **L7**, (△) **L8**.

elsewhere in connection with the dielectric behaviour of oligomers in general [11]. In all cases a stepwise decrease of $f_{R\parallel}$ at the N/is transition and a higher activation energy in the S_A phase were detected.

Furthermore, it should be pointed out that the f_R values in the isotropic phase of **L6, L7** and **L8** are nearly the same (about 90 kHz at 357 K) and 1/20 of the $f_{R\parallel}$ value found for the mesogen **M** (1·8 MHz). For all three linear compounds, in both directions, an α-mechanism was found which had the highest intensity in the perpendicular direction. Experimental data are presented in the 3D plot in figure 7. The relaxation frequency of the α-process amounts to about 90 kHz at 294 K for all homologous, linear oligomers. The corresponding reorientation around the molecular long axis of the mesogen **M** is about five times faster. All these experimental data are summarized in figure 8. It should be emphasized that the high frequency local β-relaxation, which could be clearly detected only in **L7**, should be observed for all compounds [12, 13].

In the investigated temperature and frequency range, the reorientation of the longitudinal dipole of the liquid crystalline unit (δ-relaxation) follows a simple Arrhenius relation. The high frequency α-relaxation, which is mainly related to the reorientation of the perpendicular dipoles, shows WLF behaviour [14]. Both mechanisms are well separated in the isotropic phase, too.

In contradiction to measurements described before, cyclic siloxanes could not be oriented completely. Slow cooling and repetition of the cooling procedure only results in a partial orientation. Experimentally obtained absorption maxima are for **C6** at $T = 345$ K, $\varepsilon''_{zz} = 0{\cdot}544$ and $\varepsilon''_{xx} = 0{\cdot}244$. Assuming the same degree of order S_d for the macroscopic orientation of the different preferred axis in relation to the laboratory coordinates, z and x respectively, as given by Attard *et al.* [9], one can obtain for the measured dielectric absorption intensities of the δ-relaxation in the direction of the magnetic field (z) and perpendicular to it (x):

$$\varepsilon''_{zz} = \tfrac{1}{3}\varepsilon''_\parallel(1 + 2S_d) \qquad (2a)$$

$$\varepsilon''_{xx} = \tfrac{1}{3}\varepsilon''_\parallel(1 - S_d) \qquad (2b)$$

Using the abbreviation $\varepsilon''_{zz}/\varepsilon''_{xx} = Q$, the macroscopic degree

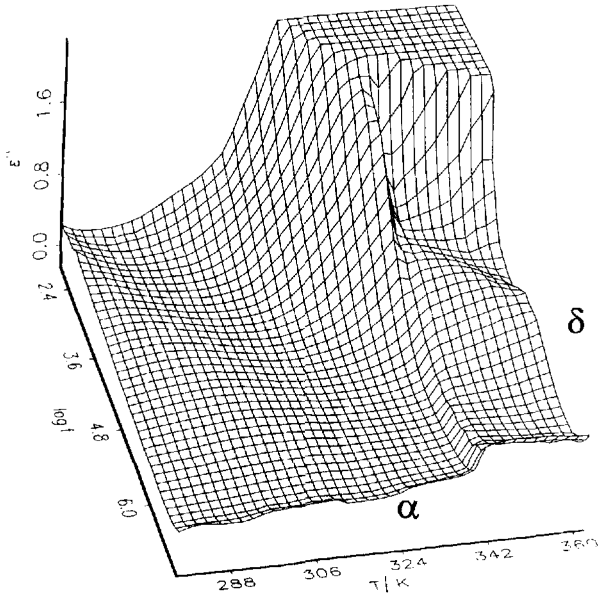


Figure 7 3D plot of the dielectric absorption ε'' of **L7** in the parallel direction.

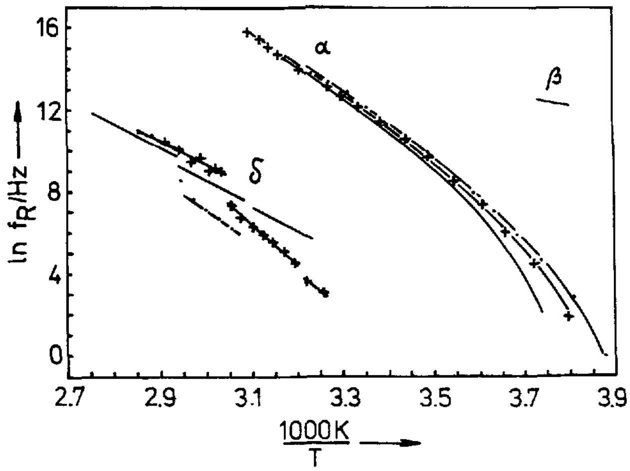


Figure 8 Arrhenius plots of the relaxation frequencies for linear oligomers: (+) **L6**, (●) **L8**, (–) **L7** the only curves without experimental points. The α and β-relaxations were measured only for the S_A phase, the δ-process for the is, N and S_A phases for **L6** and **L7**, and for the is and N phase for **L8**.

of order in the preferred direction (*z*) can be calculated according to

$$S_d = (Q - 1)/(Q + 2). \quad (3)$$

$\varepsilon''_{\|}$ is the value which should be obtained for complete orientation ($S_d = 1$). Using the given experimental data, $\varepsilon''_{zz}/\varepsilon''_{xx} = 2{\cdot}2$ was calculated. From this relation a degree of order for the $S_d = 0{\cdot}29$ was estimated for the domains. In

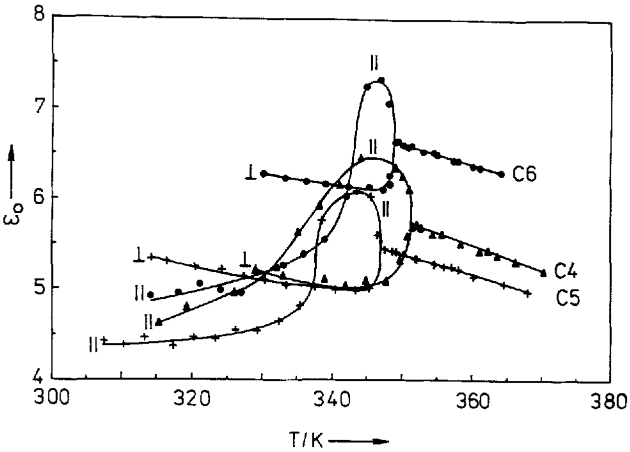


Figure 9 Static dielectric constants of the partially oriented cyclic siloxanes (▲) **C4**, (+) **C5** and (●) **C6**.

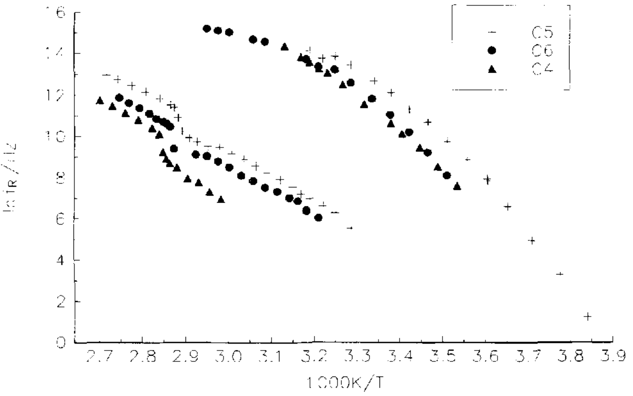


Figure 10 Arrhenius plots for the cyclic siloxanes: (▲) **C4**, (+) **C5**, (●) **C6**.

relation to this small ordering of the domains, only the general behaviour of the static dielectric constants should be discussed. On the other hand, the dielectric relaxation frequencies of the δ- and α-process are separated by about three decades from each other, and therefore the relaxation frequencies are not so strongly affected by the macroscopic disorientation effect, as shown in the experiments by Attard *et al.* [9], or Bormuth and Haase [15]. As mentioned above, the static dielectric behaviour of **C6** in the liquid crystalline phases should be regarded only as a preliminary result, but the general behaviour—the strong decrease of $\varepsilon_{\|0\mathrm{i}}$ with decreasing temperature—is well reflected (see figure 9).

Conductivity, incomplete orientation and the decreasing absorption intensity with decreasing temperature do not allow us to calculate the relaxation frequencies of the δ-relaxation down to low temperatures. Therefore, in the survey of the relaxation frequencies (see figure 10) only the α-relaxations are given over a wide temperature and frequency range.

4. Discussion

For a comparison, the dielectric data for the isotropic phase are summarized in table 3. Let us discuss first the relaxation frequencies. Generally, the relaxation frequency of the mesogenic side group precursor **M** is about one decade higher than that of the oligomers. By comparison of analogous linear and cyclic siloxanes, one cannot detect a big difference between these two groups of siloxanes. Furthermore, there is no indication of a systematic change in the f_R values as in substituted polyethylenes, with increasing degree of polymerization [5]. Therefore, one has to conclude that (i) the siloxane main chain is much more flexible (see also [16]) and (ii) the big mesogenic side group shows lower relaxation frequencies. In this way, the dynamics of the presented oligomers is dominated by the mobility of the mesogenic side group and small differences in the way it packs. The detected step in f_R at the N–is transition and practically no change of f_R at the N–S_A and S_A–S_C phase transitions are in agreement with data on other samples [2]. Furthermore, the α-relaxation of the cyclic and linear siloxanes do not show big differences, indicating an effect of the comparable chemical structures and glass temperatures of the samples under discussion.

Interesting relations can be obtained by comparison of the static dielectric constants in the isotropic phase, as shown in table 3, and the plotted data in figure 11. Referring to table 3, we can point that there are bigger differences between the static dielectric constants of the monomer **M** and the oligomers in the isotropic phase. This result must be caused by the dipole moment of the siloxane main chain. As shown in figure 11 for **L6** in the nematic phase, the relative increase of $\varepsilon_{0\parallel}$ with respect to the monomer is bigger than that of $\varepsilon_{0\perp}$. Therefore, in relation to the chemical structure of the siloxane main chain, one can conclude that the dipoles of the main chain act more in the direction of the parallel oriented side groups. In other words: the main chain is oriented preferably perpendicular to the side group.

Table 3. Static dielectric constants and relaxation frequencies at $T = 360$ K (isotropic phase).

Compound	$\varepsilon_{0,\text{is}}$	f_R/MHz
M	4·63	1·33
L6	5·83	0·23
L7	6·10	0·12
L8	6·38	0·16
C4	5·55	0·06
C5	5·17	0·26
C6	6·43	0·10

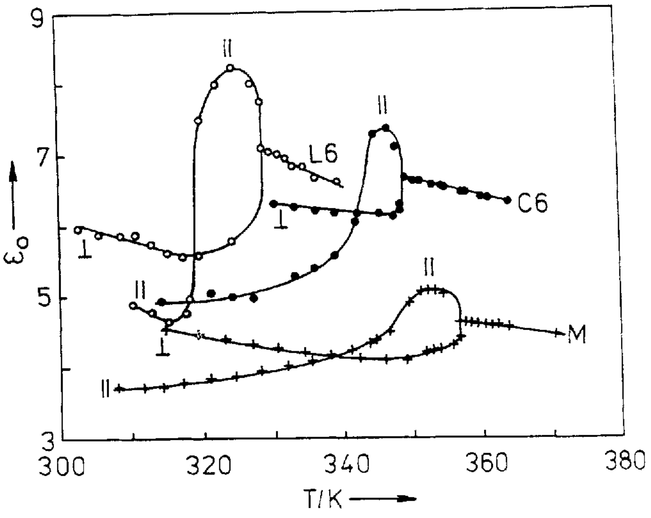


Figure 11 Static dielectric constants for the mesogenic side group precursor (+), **M** (●) **C6** and (○) **L6**.

The decrease of $\varepsilon_{0\parallel}$ in the nematic and smectic A phase is much more interesting. If one compares figures 4 and 6 where the samples were well oriented in the linear siloxanes, a quite strong decrease of $\varepsilon_{0\parallel}$ with decreasing temperature can be recognized. It should be pointed out that the decrease of the static dielectric constant already started in the isotropic phase, becomes stronger in the nematic state and reaches its highest intensity in the smectic A phase. A corresponding increase of $\varepsilon_{0\perp}$ could not be detected. Therefore, one has to consider that the Y-shaped liquid crystalline molecules are oriented antiparallel in the short range. If now these molecules are fixed *via* a spacer on to the siloxane backbone, they show a much stronger tendency to form antiparallel oriented aggregates. The observed effects, especially the change of $\varepsilon_{0\parallel}$ with decreasing temperature, are much stronger as discussed by Scheuermann *et al.* [17], in the case of a dipolar correlation without steric contributions. In the pretransitional range of the nematic to smectic phase transition, the linearly connected, Y-shaped liquid crystalline molecules form a kind of two-dimensional molecular 'zip-fastener' [18] which becomes 'closed' in this temperature range. A schematic representation of this effect is sketched in figure 12.

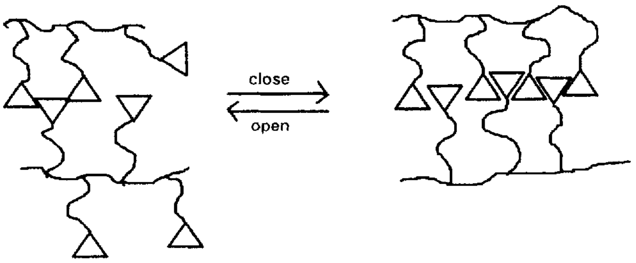


Figure 12 Sketch of the two-dimensional 'zip fastener'.

With increasing temperature, the opposite dielectric behaviour was found which can be interpreted as the 'opening' mechanism.

We are indebted to Dr F. H. Kreuzer (Consortium für Elektrochemische Industrie GmbH, München) and Dipl. Chem. A. Hohmuth (Max-Planck-Arbeitsgruppe Flüssigkristalline Systeme, Halle) for supporting the synthetic work. The authors are also grateful to the Darmstadt liquid crystal group (Professor W. Haase) for help in construction of the equipment and to the DFG for financial support.

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