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## Liquid Crystals

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# Dielectric behaviour of two dimeric liquid crystalline siloxanes

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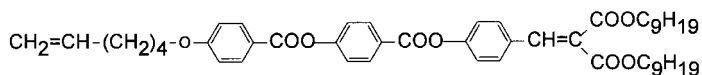
The temperature and frequency dependence of their dielectric constants have been investigated for two dimers consisting of swallow-tailed terminal groups connected via siloxane central parts of different length. The results have been compared with those of the respective monomer. The central part contributes in different ways to the static dielectric constants in the isotropic phase. From relaxation measurements, it can be concluded that the reorientation process about the short axis of the terminal groups is comparable with the respective process in monomers. The relaxation frequencies as well as intensities are almost uninfluenced by the siloxane part which suggests a very flexible structure of such dimers. Unfortunately, the maintenance of the antiparallel arrangement of swallow-tailed parts of the dimers could not be proved because of insufficient material for experimental work on the  $S_A$  phase.

## 1. Introduction

After a period in which much research work had been done in the field of monomer and polymer liquid crystals, materials taking a position in between monomers and polymers are now the object of many scientific papers [1–11]. Such materials are helpful in understanding the dependence of physical properties on the degree of polymerization and in studying the influence of a changing environment on molecular motions. In this work, two dimers, **Si2** and **Si12**, have been synthesized, investigated and compared with the monomer **M** and the siloxane precursor **P<sub>x</sub>**. Phase transition temperatures are given in degrees Celsius.

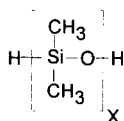
For several years it has been known that Y-shaped so-called swallow tailed liquid crystal materials have a pronounced tendency to adopt an antiparallel arrange-

ment in the short range [12]. This particular feature has been carefully investigated by dielectric measurements, including the influence of molecular structure, dipolar interactions and polymer backbones [13–15]. Recently, it was shown by Schiewe and Kresse [9–11] that in linear and cyclic siloxanes with swallow-tailed side chains, the tendency to the antiparallel arrangement of the side chains is not suppressed. In order to fill the gap between the monomer on the one hand and the oligomers on the other, dimers of swallow-tailed molecules connected via Si-units have been investigated. Thereby, it was hoped that two questions would be answered: (i) to what extent does the central part influence the dipolar reorientation and antiparallel arrangement of the mesogenic parts; (ii) in which way are the mesogenic units mutually orientated in terminally connected dimers?



**M**

Cr 71 ( $S_C$  41)  $S_A$  79 N 86 I

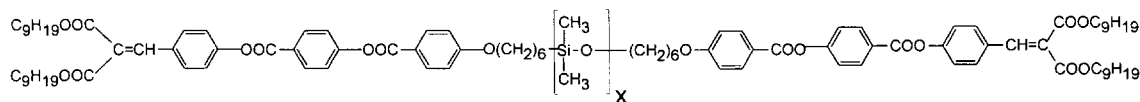


$x = 2$

**P<sub>x</sub>**

$x = 12$

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**Si<sub>x</sub>** $x = 2$ **S<sub>A</sub> 40 N 65 I** $x = 12$ **S<sub>A</sub> 56 I**

## 2. Experimental

### 2.1. Synthetic section

The synthesis of the monomer is described elsewhere [10]. Siloxane precursors were purchased from the E Merck (**P2**, purity 96%) or supplied from Wacker Chemie (**P12**, purity 90%). The siloxanes **Si2** and **Si12** were obtained by a hydrosilylation reaction [16] of **M** with the respective precursor in toluene ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  as catalyst, 48 h at 100°C). The crude product was purified by column chromatography on silica gel (Baker, 40  $\mu\text{m}$ ) with toluene/chloroform (1:1.5) as eluent. After evaporating the solvents, the sample was dissolved in chloroform and again eluted through a short column of  $\text{Al}_2\text{O}_3$  (E Merck, neutral, 0.063–0.200 mm). The last procedure involved a filtration using a PTFE filter with a pore size of 0.2  $\mu\text{m}$  and the evaporation of the solvent (24 h, 60°C *in vacuo*). All of these steps were necessary in order to reduce the conductivity of the samples. The yields were 28% (**Si2**) and 38% (**Si12**).

The following NMR signals were detected:

**Si2**  $^1\text{H}$  NMR: (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.01 (s, 6H, 2x Si- $\text{CH}_3$ ), 0.47–0.52 (t, 2H, Si- $\text{CH}_2$ - $\text{CH}_2$ -), 0.84–0.87 (t, 6H, 2x  $\text{CH}_3$ - $\text{CH}_2$ -), 1.14–1.32 (m, 30H, Si- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>3</sub>- $\text{CH}_2$ - $\text{CH}_2$ -O, 2x  $\text{CH}_3$ ( $\text{CH}_2$ )<sub>6</sub>- $\text{CH}_2$ - $\text{CH}_2$ -O), 1.58–1.70 (m, 4H, 2x COO- $\text{CH}_2$ - $\text{CH}_2$ -), 1.76–1.83 (t, 2H, - $\text{CH}_2$ - $\text{CH}_2$ -O-), 3.97–4.04 (t, 2H,  $\text{CH}_2$ - $\text{CH}_2$ -O-), 4.19–4.28 (t, 4H, COO- $\text{CH}_2$ - $\text{CH}_2$ -), 6.92–8.27 (several m, 12H, Ar), 7.70 (s, 1H, - $\text{CH}=\text{C}$ ).

**Si12**  $^1\text{H}$  NMR: (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.06 (s, 36H, 12x Si- $\text{CH}_3$ ), 0.53–0.57 (t, 2H, Si- $\text{CH}_2$ - $\text{CH}_2$ -), 0.87–0.90 (t, 6H,  $\text{CH}_3$ - $\text{CH}_2$ -), 1.17–1.35 (m, 30H, Si- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>3</sub>- $\text{CH}_2$ -O, 2x  $\text{CH}_3$ ( $\text{CH}_2$ )<sub>6</sub>- $\text{CH}_2$ - $\text{CH}_2$ -O), 1.53–1.71 (m, 4H, 2x COO- $\text{CH}_2$ - $\text{CH}_2$ -), 1.79–1.93 (t, 2H,  $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 3.98–4.04 (t, 2H,  $\text{CH}_2$ - $\text{CH}_2$ -O-), 4.23–4.30 (t, 4H, COO- $\text{CH}_2$ - $\text{CH}_2$ -), 6.94–8.25 (several m, 12H, Ar), 7.70 (s, 1H, - $\text{CH}=\text{C}$ ).

### 2.2. Dielectric section

The dielectric measurement device is a Hewlett-Packard impedance analyser HP4192A (10 Hz–10 MHz) piloted by a computer which allows automatic measurements of the complex permittivity,  $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ , of the sample. The measuring cell is a capacitor ( $A = 1 \text{ cm}^2$ ,  $d = 0.2 \text{ mm}$ ) whose temperature can be varied

from  $-15^\circ\text{C}$  to  $170^\circ\text{C}$  by means of a Eurotherm control device. By switching on a magnetic field (0.7 T), the parallel ( $E \parallel B$ ) and perpendicular ( $E \perp B$ ) component of  $\varepsilon^*$  can be determined if the substance possesses a nematic phase (**M**, **Si2**). In order to obtain the static dielectric constants  $\varepsilon_0$ , relaxation frequencies,  $f_R$  and parameters  $h$ , the experimental data,  $\varepsilon'(f)$  and  $\varepsilon''(f)$ , have been fitted to modified Cole–Cole equations [17]. The Cole–Cole parameter  $h$  amounts 1 in the case of ideal Debye relaxations. The contribution of the conductivity to the overall loss is taken into account by the term  $A/f$ . As sample conductivity complicates or prevents the investigation of relaxation processes in many cases, much effort was given to minimizing this problem during the purification procedures.

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

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

## 3. Results and discussion

Experimental curves for **Si2** and **Si12** are presented in figure 1. There are two relaxation ranges for both substances. Because of the small frequency window and the high conductivity (see the increase of  $\varepsilon''$  at the low frequency side of the loss curves), the low frequency relaxation can only be observed in the isotropic phase and the liquid crystalline phase as it forms, and the second relaxation in the  $S_A$  phase.

Figure 2 shows the temperature dependence of the static dielectric constants for **Si2**, **Si12**, and **M** [10]. The siloxane precursor **P12** has a dielectric constant of about 2.2 (26°C) in the frequency range investigated. Comparing the static dielectric constants in the isotropic phase, one establishes a surprising fact. The dimer **Si12** has almost the same  $\varepsilon_{0,I}$  as the monomer. The values of both substances lie on a line. In contrast,  $\varepsilon_{0,I}$  of **Si2** is

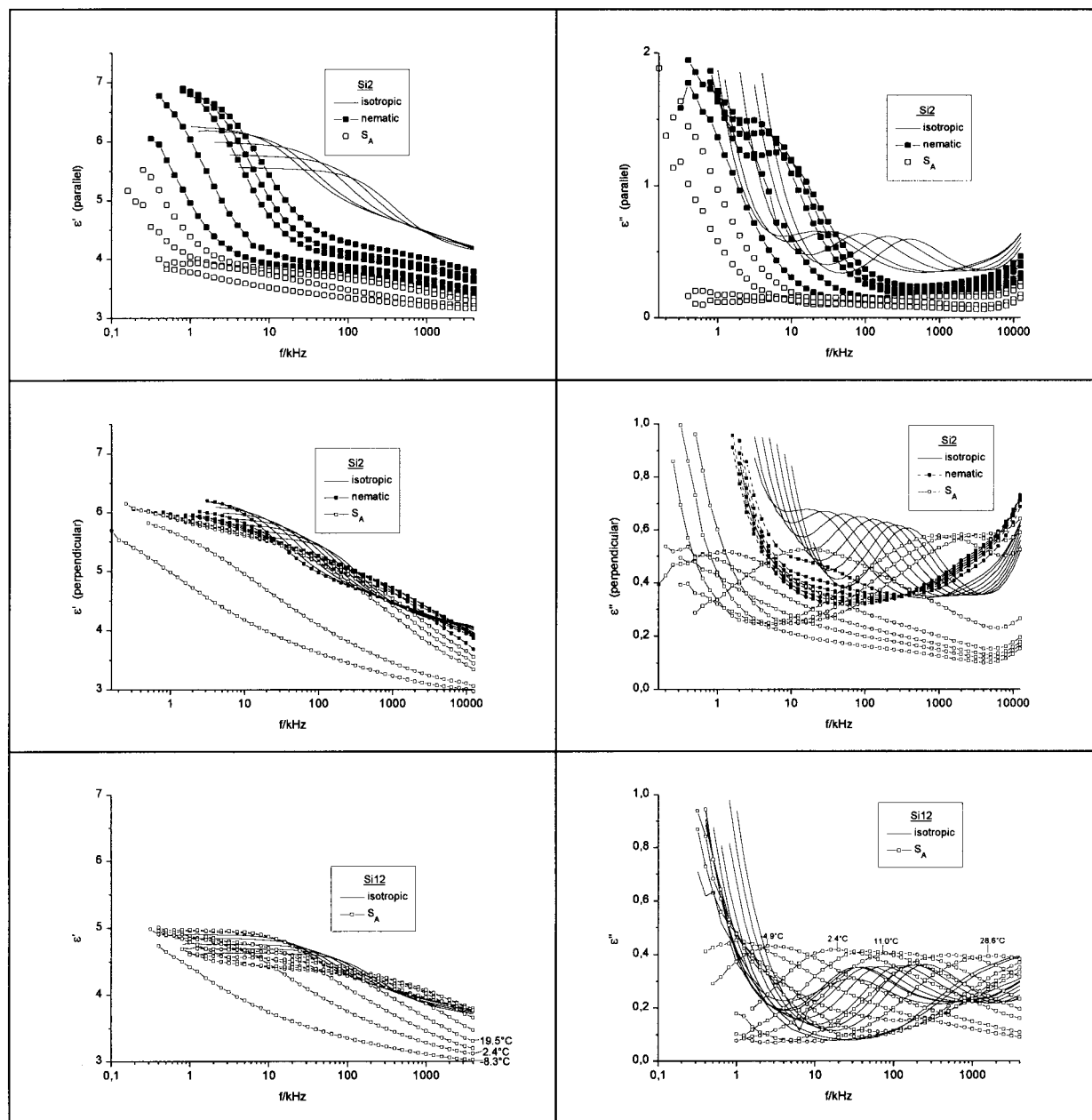


Figure 1. Experimental curves  $\epsilon'(f)$  and  $\epsilon''(f)$  of **Si2** and **Si12** at several temperatures. Because of the absence of nematic phase in **Si12**, measurements for different orientations (parallel, perpendicular) were not possible.

about 40% higher than that of **M**. Investigations on linear and cyclic oligomers [9] (siloxane backbone with swallow-tailed side groups) have provided in all cases significantly higher values of  $\epsilon_{0,I}$  compared with the monomer. This finding had been explained by a contribution of the dipole moment of the siloxane part. As every Si atom is connected to a side chain, the freedom of movement of the backbone is restricted and the dipole moment of the Si–O bonds contributes to that of the side chain. This argument is valid for **Si2**, also.

Corresponding with this explanation, the  $\epsilon_{0,I}$  values of ‘diluted’ polymers drop with increasing ‘dilution’ [11]. From the relatively small  $\epsilon_{0,I}$  of the precursor **P**, this would suggest that the Si–O dipoles partially compensate each other. This situation changes on substitution of H atoms by mesogenic side groups, especially if each Si atom bears a side group (**Si2**, [9]). In **Si12** the siloxane part is quite long and the Si–O dipoles in the middle part behave like those in **P** and do not essentially contribute to the dipoles of the mesogenic group.

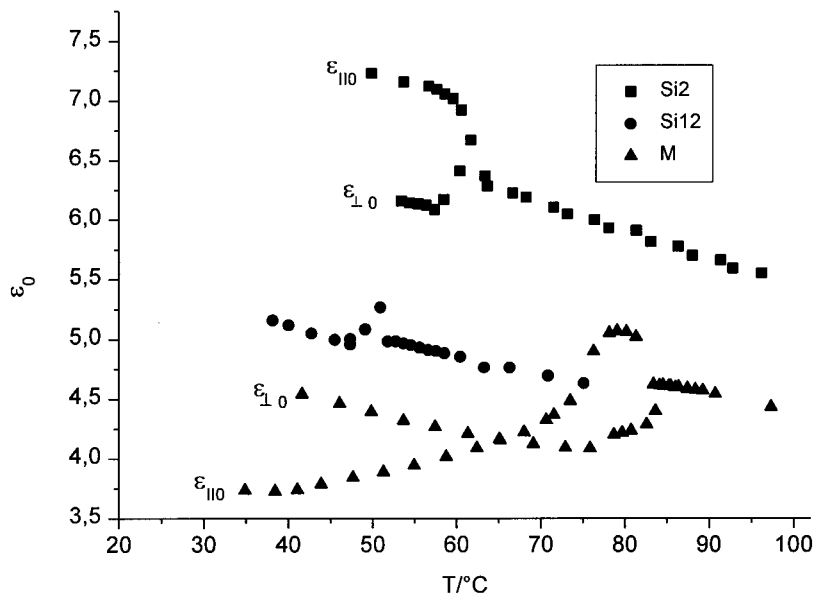


Figure 2. Static dielectric constants of **Si2**, **Si12** and **M** for comparison.

We are not able to prove the tendency to an antiparallel arrangement in the dimers as we do not have enough experimental data at the transition  $N/S_A$ . But, from the decrease of the absorption intensity (figure 1) at this transition, we assume the maintenance of the antiparallel correlation in the dimers.

The results of relaxation measurements are summarized in the Arrhenius diagram (figure 3) and the table. The low frequency process 1 is caused by reorientation motions of the swallow-tailed part about the short axis. As this relaxation mechanism is related to the longitud-

inal component of the dipole moment, it can only be observed in the liquid crystalline phases for parallel orientation of electric field and molecular director. **Si2** possesses in the isotropic, as well as in the liquid crystalline phases, the lowest  $f_{R1}$  values which suggests the lowest flexibility of this motion. This agrees with the above mentioned influence of the siloxane part on the dielectric behaviour. In **Si12**, the siloxane part also causes the decrease in  $f_{R1}$ , but not to the same extent as in **Si2**.

The nature of the high frequency relaxation 2 is more

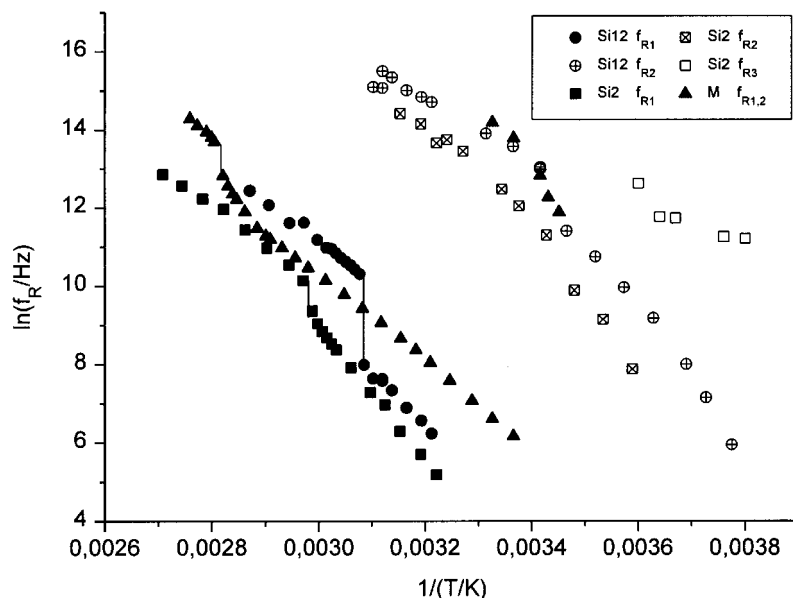


Figure 3. Arrhenius plots of **Si2**, **Si12** and **M**. The lines designate the phase transitions isotropic/liquid crystalline and indicate steps in  $f_{R1}$ . The relaxation frequencies  $f_{R2}$  have been obtained by fitting the broad adsorption curves to one relaxation process.

Table. Summary of the results obtained by relaxation measurements.  $E_A$  = activation energy,  $p$  = change in relaxation frequencies,  $h$  = Cole–Cole parameter,  $\epsilon_{01}-\epsilon_{02}$  = dielectric increment, \* = measured for a parallel orientation.

Parameter	M	Si2	Si12
$p = \frac{f_{R1}(I)}{f_{R1}(LC)}$	2.5	2.0	10
$E_{A1}(I)/\text{kJ mol}^{-1}$	100	$80 \pm 3$	$85 \pm 2$
$E_{A1}(LC)/\text{kJ mol}^{-1}$	$90 \pm 2$	$140 \pm 5$	$112 \pm 4$
$h_1(LC)$	1	0.85	0.90
$(\epsilon_{01}-\epsilon_{02})_I$	1.2	1.4	0.8
$(\epsilon_{01}-\epsilon_{02})$ at $T_{1/LC} - T = 4 \text{ K}$	2.1*	3.0*	0.65
$h_2(LC)$	0.8	0.6	0.7

complex as can be seen from the broadened and increasingly asymmetric absorption curves. It is caused by the reorientation about the long axis and, additionally, by motions of the siloxane part. This relaxation mechanism is easily detectable for a perpendicular orientation of the electric field and director, as can be seen in figure 1 by comparing the loss curves of **Si2**. There is no linear dependence of the relaxation frequencies on the inverse temperature. That is why the data have been fitted to the Vogel–Fulcher–Tamman equation [18–20] and the following  $T_0$  values at which this reorientation process is frozen out have been obtained:  $T_0(\text{Si12}) = -51^\circ\text{C}$ ,  $T_0(\text{Si2}) = -35^\circ\text{C}$ . This characteristic temperature is usually about 40 K lower than the glass transition temperature determined by DSC measurements between  $-20^\circ\text{C}$  and  $20^\circ\text{C}$ .

A detailed analysis of the temperature dependence of the Cole–Cole parameter  $h$  with considerations of the asymmetry is not possible because the high frequency side of the loss curves could never be measured completely. As a rough rule, the decrease of  $h$  and asymmetry can be established. As an example the absorption curves at lower temperatures of **Si2** have been analysed as the sum of two Cole–Cole relaxations. The same procedure could be carried out for **Si12**. The estimated relaxation frequencies of the third process are also given in figure 3. From the relative positions in the frequency and temperature scale, the detected relaxation mechanisms can be designated as  $\delta$  (1.process),  $\alpha$  (2.process) and  $\beta$  (3.process) [21]. The results of the relaxation measurements are of interest for all dimers connected via a flexible spacer.

(i) There are only small differences between the relaxation frequencies ( $f_{R1}$ ) of **M**, **Si2** and **Si12**. Even the existence of the low frequency relaxation and the step of  $f_{R1}$  at the transition I/LC indicate a relatively independent reorientation of the liquid crystalline units.

(ii) The dielectric increment  $\epsilon_{01}-\epsilon_{02}$  is a measure for the number of reorienting molecular dipoles. Although, a smaller increment is to be expected for **Si2** than for **M**, the opposite has been found. The dimer **Si2** does have a larger increment (see the table). This means that the short siloxane central part does not hinder the reorientation of the terminal groups about their short axis. Possibly, the large increment suggests a lower tendency to antiparallel arrangement in **Si2** compared with **M**.

This experimental result does not support the model of phase separation [2] or sketches made from X-ray data [3]. The suggested models should be improved in such a way that the reorientations of liquid crystalline units about the molecular short axis are possible.

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