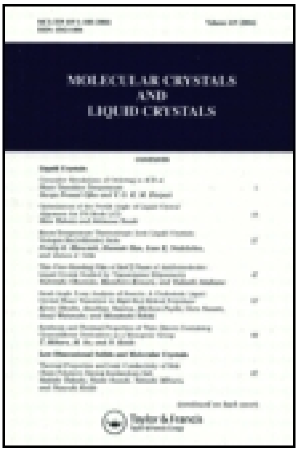

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Comparative Dielectric Investigations of Liquid Crystalline Oligomers and Monomers

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COMPARATIVE DIELECTRIC INVESTIGATIONS OF LIQUID CRYSTALLINE OLIGOMERS AND MONOMERS

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Abstract Dielectric relaxation times and the static dielectric behaviour of monomers and oligomers with definite chemical structure are compared with each other.

INTRODUCTION

Recently Novotna et al.[1] could demonstrate that the dielectric relaxation frequencies of cyanobiphenyl in poly-{1-[5-(4'-cyano-4-biphenylyloxy)hexyloxycarbonyl]ethylene} strongly depend on the degree of polymerization. As shown in Fig. 1 the relaxation frequency f_{RII} for the reorientation of the liquid crystalline unit around the short molecular axis (δ-relaxation) decreases in the oligomer range and reaches a saturation value at higher degree of polymerization characterized by the mean value P_w (w-weight).

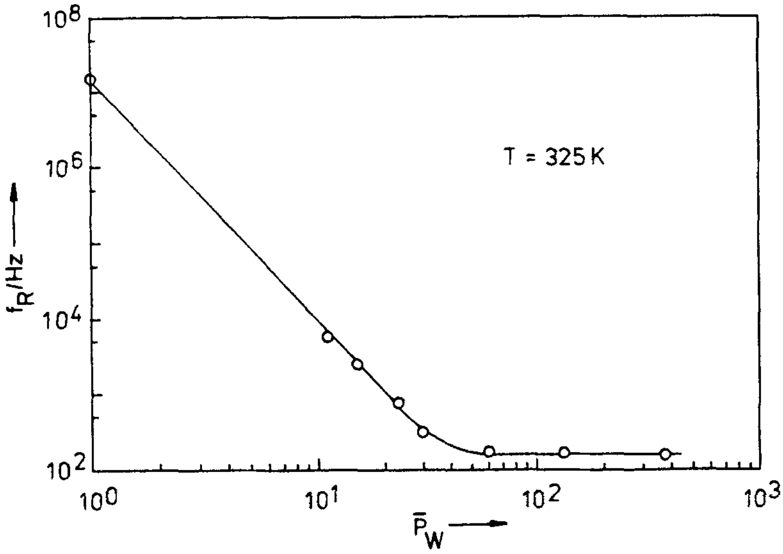


Fig. 1 Relaxation frequency f_{RII} versus the mean degree of polymerization P_w

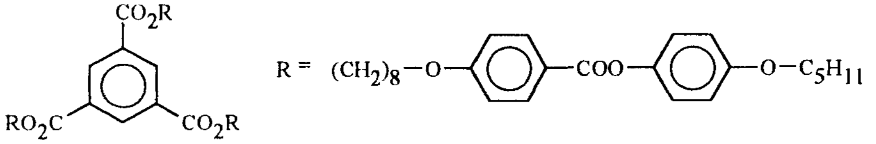
The disadvantage of the results under discussion was that the samples have had a distribution of the molecular weight. Therefore, we were interested to investigate oligomers with a definite molecular structure and to compare the data with results on the respective monomeric liquid crystals.

EXPERIMENTAL PART

The dielectric measurements were carried out in a metal capacitor (d=0.20 mm, A~1 cm^2). The cell was calibrated with cyclohexane. Using a magnetic field of H=0.7 T the samples could be oriented at the phase transition into the nematic (N) state. A HP4192A impedance analyzer (1kHz-10MHz) and a SI 1260 Solartron Schlumberger in combination with a Chelsea Interface (10^{-3} Hz-1MHz) were applied to measure capacity and loss. The samples were dried over some hours at about 340 K in a vacuum of about 1 Torr in order to reduce the conductivity.

RESULTS

At first two derivatives of 1,3,5-benzenetricarboxylic acid were investigated. Sample B1 could be supercooled to room temperature and storred for weeks without crystallization.



B1

cr 368 (S$_A$ 366) N 376 I (temperature in K)

The respective monomer M1 with an octyloxy-group additionally shows a smectic C phase (cr 329 S$_C$ 335 S$_A$ 337 N 358 I) which could not be detected in B1. Relaxation frequencies for the reorientation around the short ($f_{R\parallel}$) and the long ($f_{R\perp}$) molecular axis are presented in Fig. 2. A dielectric increment of $\Delta_{\parallel}$=0.24 and a Cole-Cole distribution parameter^2 of h=0.20 were detected in the nematic phase of the oligomer B1 for the low frequency $f_{R\parallel}$ values. At the transition into the S$_A$-phase $\Delta_{\parallel}$ decreases stepwise to 0.18 whereas h seems to be constant inside of the experimental error of Δh=±0.03. On the other hand the monomer exhibit a dielectric increment of $\Delta_{\parallel}$=0.79 and a mechanism which can be regarded as Debye relaxation (h=0.01).

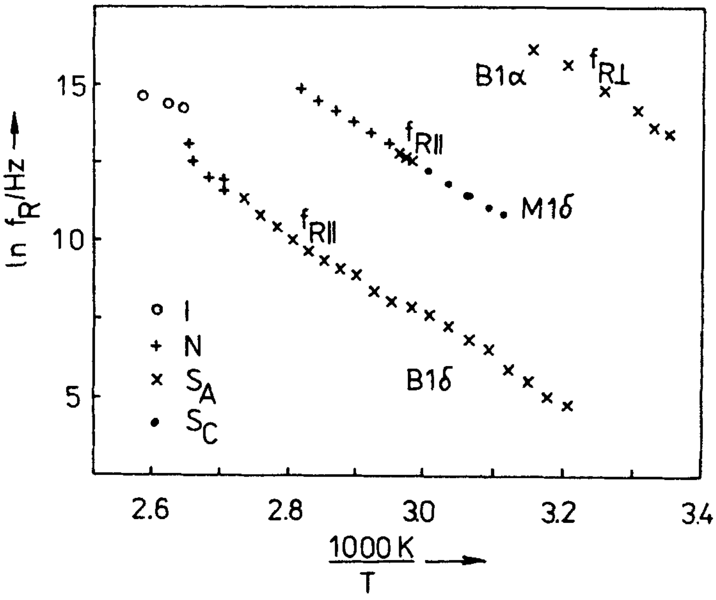


Fig. 2 Dielectric relaxation frequencies of the oligomer B1 and the respective monomer M1 as function of the reciprocal temperature

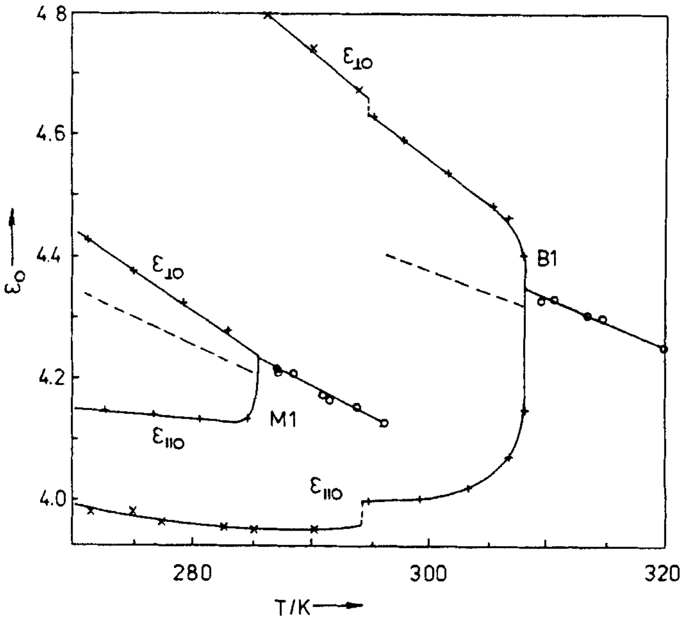


Fig. 3 Static dielectric constants of B1 and M1 at different temperatures
--- mean dielectric constant

Furthermore a stepwise increase of $f_{R\parallel}$ of B1 at the transition into the isotropic state and a $6 \cdot 10^4$ times faster reorientation around the long molecular axis $f_{R\perp}$ ($\Delta_\perp$=2.7, h=0.5) could be measured). Activation energies of 111 kJ mol^{-1} ($f_{R\parallel}$, S_A) and 120 kJ mol^{-1} ($f_{R\perp}$, S_A) of B1 and of 111 kJ mol^{-1} ($f_{R\parallel}$, N, S_C) of the monomer M1 were calculated.

The static dielectric constant of the polymer in the isotropic phase is higher than that of the monomer due to the additional dipoles of the three -COO- groups which also should be responsible for the lower dielectric anisotropy (Fig. 3). The mean dielectric constant $\varepsilon_0=1/3(2\varepsilon_{\perp 0}+\varepsilon_{\parallel 0})$ shows the same step in both, B1 and M1, indicating the same dipolar correlation in the nematic phases.

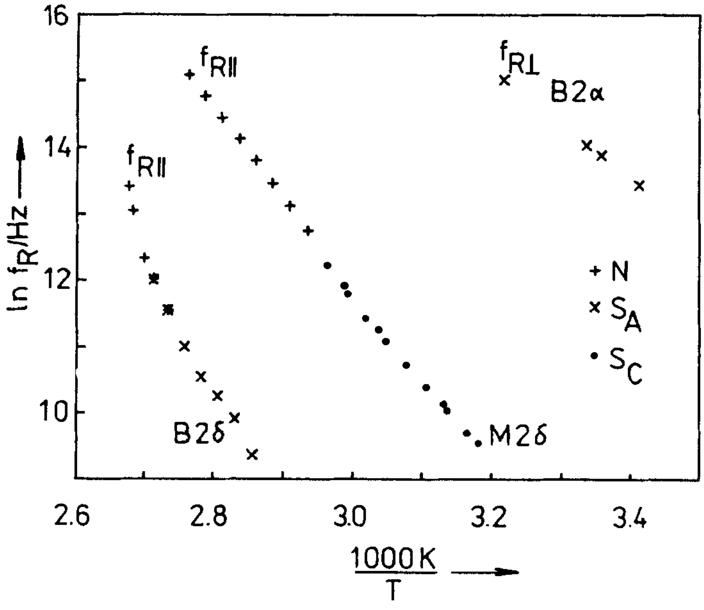
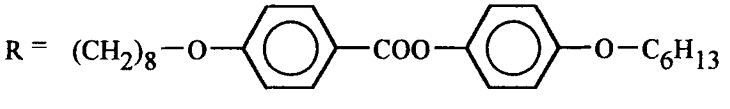


Fig. 4 Dielectric relaxation frequencies of B2 and the monomer M2

In general the similar behaviour with respect to the relaxation frequencies was measured for B2 (see Fig. 4) where the pentyloxy-group is substituted by a hexyloxy one:



B2

cr 373 (S_A 366) N 374 I

For the respective monomer M2 no S_A-phase was found: cr 326 S_C 339 N 361 I. The low frequency f_{II} of the B2 process exhibit in the nematic phase a Cole-Cole absorption (Δ_{II}=0.11, h=0.1) with the relatively high activation energy of 400 kJ mol^{-1}. In the S_A-state the absorption intensity decreases to Δ_{II}~0.06 (h=0.3) with E_A=150 kJ mol^{-1}. The high frequency absorption of the $f_{R\perp}$ process shows an activation energy of 67 kJ mol^{-1}. Again for the respective monomer M2 a Debye mechanism (h=0.01) with a dielectric increment Δ_{II}~0.8 *in the nematic phase was obtained.* (E_A(N)=110 kJ mol^{-1}, $E_A(S_C)$=102 kJ mol^{-1}). In contradiction to the former results we could measure qualitatively the same behaviour of the static dielectric constants of the oligomer and monomer as shown in Fig. 5.

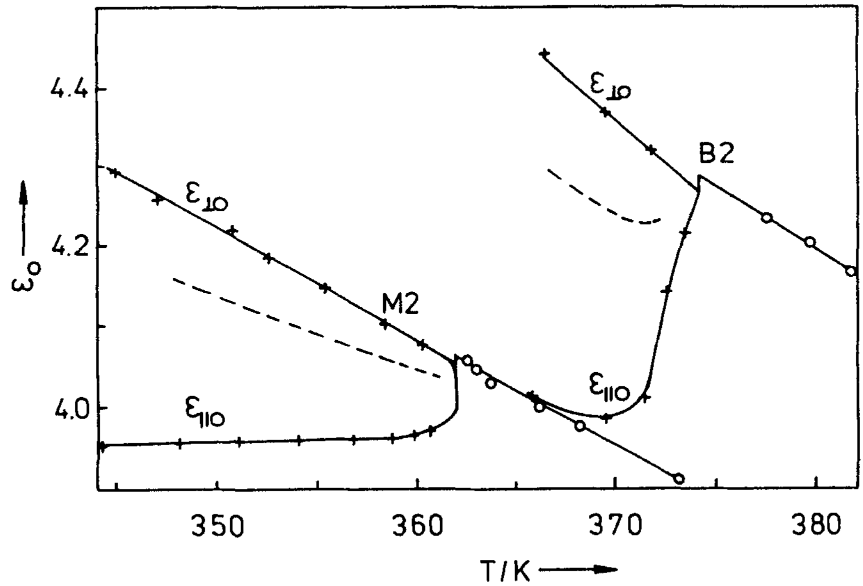
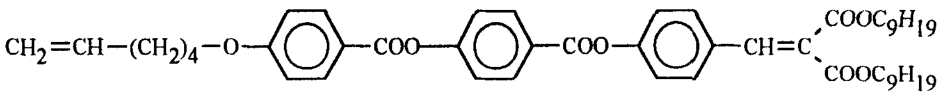
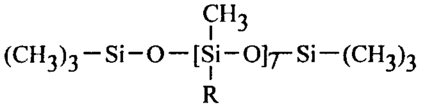


Fig. 5 Static dielectric constants of B2 and M2

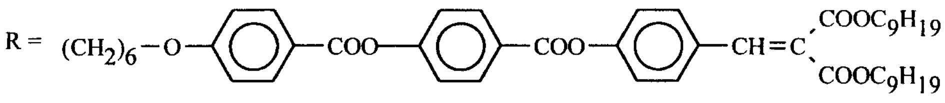
For a comparison dielectric data of the swallow-tailed monomer MS with an alkene-group at the end (cr 344 (S_C 314 S_A 352 N 359 I)



and of the respective oligomer SiS (S_A 325 N 341 I) are added.



$$(CH_3)_3-Si-O-[\underset{R}{\overset{CH_3}{Si}}-O]_7-Si-(CH_3)_3$$



S means a swallow-tailed compound for which in previous experiments[3-6] a strong tendency to an antiparallel orientation in the short range was detected . The oligomer could be oriented to about 95%. Data are presented in Fig 6.

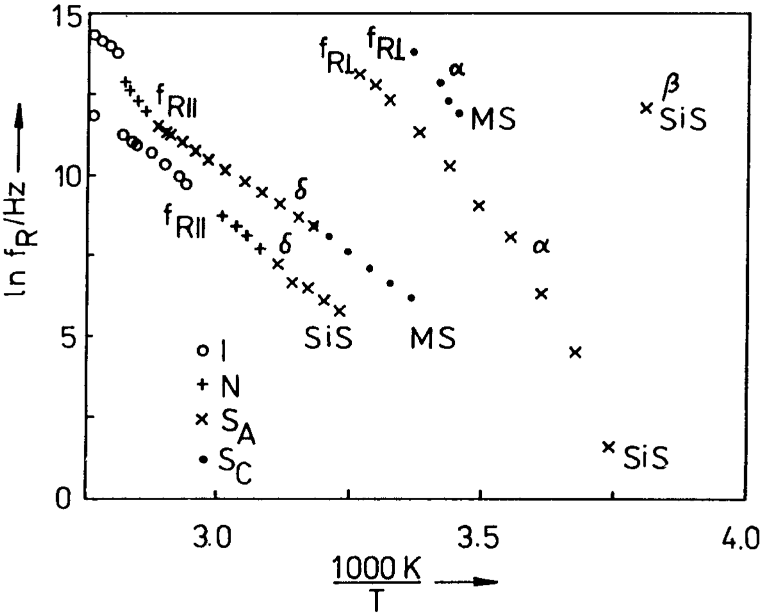


Fig. 6 Dielectric relaxation frequencies of SiS and MS

In the parallel direction a low frequency mechanism $f_{R\|}$ was found with decreasing dielectric increment especially at the N/S_A transition of SiS, I: Δ=1.84, E_A= 91 kJ mol^{-1} (355 K), N: $\Delta_{\|}$=2.05, (336 K), E_A=120 kJ mol^{-1}, S_A: $\Delta_{\|}$ =0.42, (T=324 K), E_A=99 kJ mol^{-1}. At lower temperatures the separation of the dielectric loss from the conductivity was difficult. Therefore, a simple Debye relaxation (h=0) was used for the fit. The high frequency $f_{R\perp}$ mechanism ($\Delta_\perp$=2.2, h=0.35) clearly shows a WLF behaviour. At T=322 K $f_{R\perp}$ is about 10^4 times higher than $f_{R\|}$. At lower temperatures additionally also a very broad β-relaxation (T=263 K, f_R=2·10^{5}Hz, Δ=0.29, h=0.53) could be detected. For the respective monomer MS two relaxation processes in the investigated frequency range were found. The low frequency f_{RII}-process exhibit a Debye process with a dielectric increment Δ=0.97 (360 K) and E_A=96 kJ mol^{-1}, in the isotropic and Δ_{II}=1.72 (353 K) with E_A=200kJ mol^{-1}, in the nematic state. The decrease of Δ_{II} can be clearly seen in the S_A-phase: Δ_{II}=1.72, (349 K), Δ_{II}=0.90, (320 K) where an activation energy of 86 kJ mol^{-1} was calculated. The α-mechanism (Δ=0.38, h=0.37, E_A=188 kJ mol^{-1}) could be separated only in the S_C-phase. The static dielectric constants of SiS and MS clearly show a decrease around the phase transition N/S_A (fig. 7). Thereby this decrease is much more pronounced in the oligomer and the former interpretation of this samples as molecular "zip-fasteners"[7] seems to be correct.

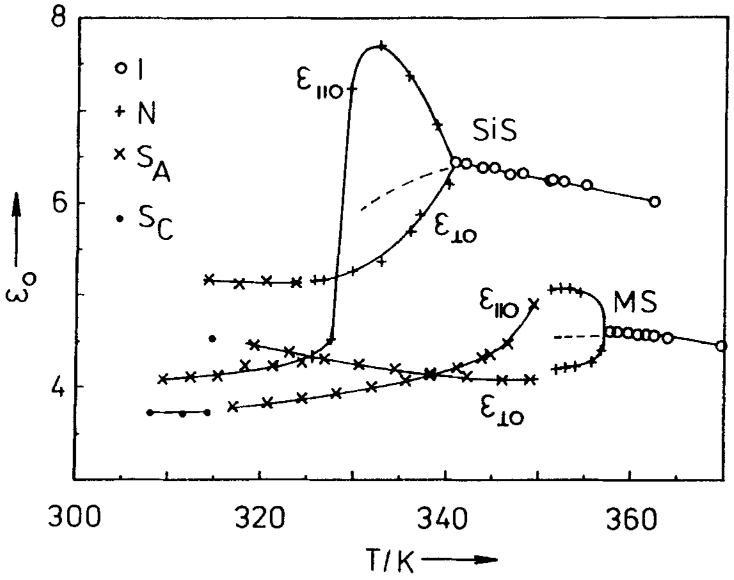


Fig. 7 Static dielectric constants of the siloxane derivative SiS and the respective monomeric alkene

DISCUSSION

The first part of the discussion should be related to the derivatives of 1,3,5-benzenetricarboxylic acid . As demonstrated in Figs. 3 and 5 the static dielectric constants of the oligomer in the isotropic phase and the $\varepsilon_{\perp o}$-values are higher than the respective data of the monomers. This effect should be connected with the dipoles of the three additional

-COO-groups. If we consider that at the given structure the dipole compounds in plane of the benzene are compensated as result of the high symmetry one has to conclude that these additional dipoles are acting only perpendicular to the plane of the 1,3,5-subst. benzenetricarboxylic fragment. From the stronger increase of $\varepsilon_{\perp o}$ with respect to the monomer (see Fig. 3) on the other hand can be concluded that these threefold substituted benzene is oriented in the same way as the other benzene molecules namely with the para axis in direction of the orienting magnetic field. Taking into account that the liquid crystal groups R are nearly parallel oriented, one has to accept a "fork-like" structure of the oligomers. This assumption is strongly supported by the dielectric increment of the Δ_{II} relaxation of component 1: Δ_{II} (M1) =0.79 and Δ_{II} (B1) = 0.24 in the nematic phase which fulfils the expected relation Δ_{II} (M1)~3Δ_{II} (B1). In the second derivative of 1,3,5-benzenetricarboxylic acid the increment of the oligomer is lower than expected: Δ_{II} (M2) =0.80 and 3Δ_{II} (B2) =0.33. This indicates a compensation of the longitudinal dipoles of the LC part in B2 by an antiparallel arrangement of different oligomers. Furthermore one has to mention that the relaxation frequencies for the reorientation around the short molecular axis f_{RII} of the monomer are about 100 times higher than that of the oligomer. This is in agreement with the expected decrease shown in Fig. 1

The swallow-tailed compound was used to show the difference in the dielectric behaviour with respect to ε_{II}. At first a clear decrase of ε_{IIo} and of the respective dielectric increment Δ_{II} with decreasing temperature was observed indicating the antiparallel correlation of the molecules in the short range. This effect is much more pronounced in the oligomer as it can be also seen at the N/S_A-transition in Fig. 7. The Y-shaped molecules of the swallow-tailed compound are much stronger antiparallel oriented in the smectic phase in comparison to that of the derivatives of 1,3,5-benzenetricarboxylic acid. This difference is caused by the molecular structure:

- the Y-shaped swallow-tailed molecules are relatively stiff in comparison with B1 and B2 in which the LC-part is connected via a spacer with the central unit.

- the flexibility of the siloxane main chain is high[8] and does allow a orientation of the LC-groups. Therefore, the relaxation frequencies of monomer and oligomer siloxanes are quite similar.

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