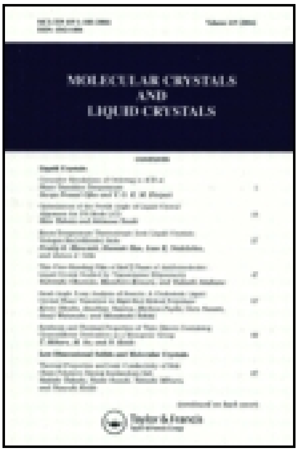

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# Synthesis and Dielectric Investigations of New Swallow-Tailed Monomers and Polymers

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A new class of liquid crystalline side chain polymers using swallow-tailed mesogens was synthesized. Comparative dielectric investigations on these polymers and on the corresponding low molecular weight substances in the frequency range from 10 Hz to 100 kHz should give information about the dynamic behaviour. The results obtained from the monomers agree well with those of other swallow-tailed liquid crystals and can be explained by an antiparallel orientation of the molecules in the $S_A$ phase. There are hints to a tendency to an antiparallel orientation of the side chains in the polymers, too.

*Keywords: synthesis, swallow-tailed monomers, polymers, dielectric investigations, antiparallel order*

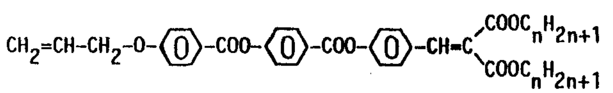
## INTRODUCTION

As already known swallow-tailed liquid crystals show a peculiarity in the dielectric behaviour: the decrease of the static dielectric constant parallel to the molecular long axis ($\varepsilon_{\|01}$) with decreasing temperature.[1,2] This effect is caused by the antiparallel orientation of the longitudinal dipole moments. Such a geometrical effect is reinforced in the $S_A$ phase where the molecules are arranged in layers. Several measurements on mixtures with swallow-tailed substances[3,4] showed that the antiparallel orientation can easily be destroyed by laterally branched liquid crystals.

The subject of this article is the synthesis of new swallow-tailed liquid crystals which can also be parts of the side chain polymers and the comparison of the dielectric data of monomers and polymers. First attempts in this direction were done by Cabrera *et al.*[5]

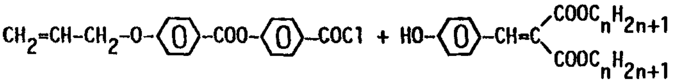
## SYNTHESIS

Analogous to the instructions by WEISSFLOG[1] the di-n-alkyl-4-(4-alkyloxy-benzoyloxy)benzoyloxy-benzylidemalonates



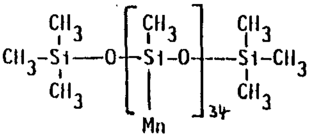
Mn n = 2,6,9,16

were obtained by acylation of di-n-alkyl-4-hydroxy-benzylidenemalonates with 4-allyloxybenzoyloxy-benzoylchlorides in methylenechloride/triethylamine.



The products were purified very carefully by fractionate crystallization until the clearing temperatures kept constant. After that the substances were purified by column chromatography.

The polymers were synthesized by hydrosilylation reactions[6] of polymethylhydrogensiloxane with the low mass mesogens in the presence of a platinum catalyst. The reactions were done in toluene at 100°C. The products were reprecipitated at first in methanol/dichloromethane and after that in benzene/hexane in order to reduce the conductivity. Furthermore the samples were dried 2 h in a vacuum of 0.1 Torr at about 400 K. Nevertheless we could not reach for all polymers low values of the conductivity. In the case of P16 the synthesis was repeated, but after the reprecipitations the conductivity was also too high in relation to the low $f_R$-values of the δ-relaxation.



Pn n=2,6,9,16

The phase transition temperatures determined by hot-stage polarization microscopy and calorimetry for polymers and monomers are shown in Table I. As already observed on the swallow-tailed substances synthesized by WEISSFLOG the tendency to form the $S_A$ phase increases with the elongation of the terminal branches.

## EXPERIMENTAL

Dielectric measurements have been performed in the frequency range from 10 Hz to 100 kHz by the aid of a modified SAWYER-TOWER-bridge.

The low molecular mass substances were measured in a silver capacitor ($A$ = 2 cm$^2$, $d$ = 0.2 mm) which was calibrated before every measurement using cyclo-

TABLE I

Phase transition temperatures (K)

| *n* | *M* | *P* | |
|---|---|---|---|
| 2 | 370 ($S_A$ 363)$N$ 430 is | [a] | $N$ 418 is |
| 6 | Cr 324 $S_A$ 370 $N$ 396 is | g 291 | $N$ 361 is |
| 9 | Cr 350 $S_A$ 358 $N$ 365 is | [a] | $N$ 334 is |
| 16 | Cr 366 ($S_A$ 362) is | Cr 318 | $S_A$ 367 is |

[a] Glassy or melting temperatures could not be clearly detected.

hexane. An orientation parallel and perpendicular to the measuring field by a magnetic field ($H \sim 0.8T$) was possible because of the low viscosity of the monomers. The error of the $\varepsilon'$ values amounts 5% and of the $\varepsilon''$ values up to 10%.

In the case of the polymers the calibration of the capacitor (a sandwich cell) was not possible because the samples could not be filled into the cell by surface forces due to its high viscosity. At $T > 450$ K chemical decomposition can be expected. Therefore, from the measured capacity $C'$ and resistance $R$ the loss $C''$

$$C'' = (2\pi f R)^{-1} \qquad f = \text{frequency}$$

was calculated as reported previously.[7]

At higher temperatures small changes of the cell distance and the area covered by the sample were possible. That's why, the qualities $C'$ and $C''$ could not be reproduced for one substance. However, the relaxation frequencies and its dependence on the temperature are not influenced by the cell geometry.

Microscopic investigations of the samples in the sandwich cell show a tendency to a homeotropic orientation expecially for P9. An improvement of the orientation by cooling in low frequency electrical fields could not be achieved.

## RESULTS AND DISCUSSION

The dielectric properties of the monomers are very similar to those swallow-tailed substances synthesized by WEISSFLOG.[1,2] The static dielectric constants $\varepsilon_{\|01}$ and $\varepsilon_{\perp 0}$ of M2, M6, M9 are depicted in Figure 1. The values of $\varepsilon_{\|01}$ were estimated from the low frequency side of COLE-COLE plots.

All investigated monomers exhibit a positive dielectric anisotropy of the static dielectric constant $\Delta\varepsilon = \varepsilon_{\|01} - \varepsilon_{\perp 0}$ in the nematic phase. $\varepsilon_{\|01}$ starts to decrease with decreasing temperature around the $N/S_A$ transition and reaches a cross over with $\varepsilon_{\perp 0}$ in the $S_A$ phase for M6 and M9. The temperature difference between the clearing and the crossover temperatures can be regarded as a measure for the tendency of the molecules to be statistically oriented. Or in other words the tendency for the antiparallel orientation decreases with increasing length of the alkyl chains $n$. May be that the antiparallel order is the driving force for the formation of the smectic $A$ layers. The monomers show a dielectric relaxation for $\varepsilon'_{\|}$ in the kHz-range which is related to the reorientation around the short molecular axis. In Figure 2 the maxima of dielectric loss are plotted versus the temperature difference ($T - T_{N/S_A}$). It can be seen that the maximal absorption intensities decrease with decreasing temperature contrary to the theory of MARTIN, MEIER, SAUPE.[8] This behaviour again is an evidence for an antiparallel arrangement of the molecules in the short range order which leads to a partly compensation of the effective dipole moment in the parallel direction.

The relaxation frequencies were fitted to the ARRHENIUS law, and activation energies of about 60 kJmol$^{-1}$ were found. The relaxation frequencies at $T = 351$ K were calculated to 25 kHz (M2), 140 kHz (M6) and 120 kHz (M9).

The investigation of the unoriented polymers was complicated due to the high conductivity and the lack of strong dipole moments. For a comparison we were

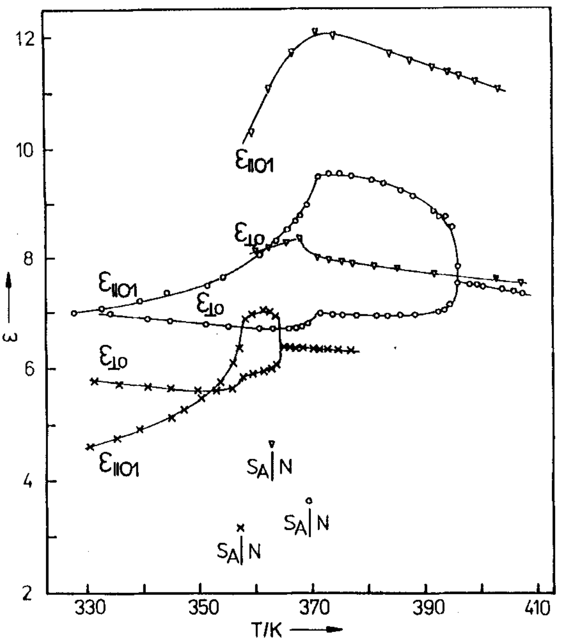


FIGURE 1 Dielectric constants of M2 (∇), M6 (o), M9 (×) versus the temperature.

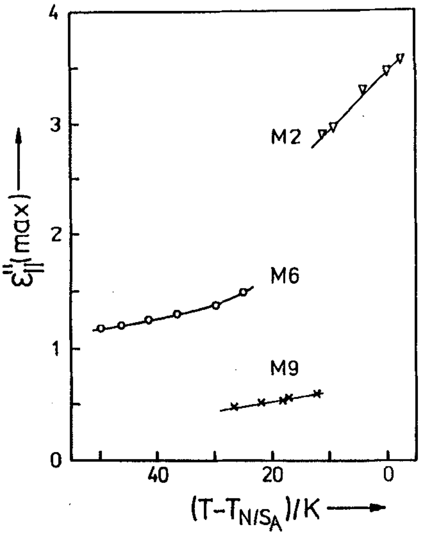


FIGURE 2 Absorption intensities of M2, M6, M9 versus the temperature difference ($T - T_{N/S}$). $2\varepsilon''_{\parallel}(\max) = \Delta = \varepsilon_{\parallel 01} - \varepsilon_{\parallel 02}$ (Debye process).

mainly interested in the low frequency relaxation process of the *LC* polymers ($\delta$) which is related to the reorientation of the side chains around the short axis. The intensity of this process is determined by the longitudinal component of the dipole moment of the mesogenic side chain.

That's why, it is to be expected that the intensity of the $\delta$-process decreases with extension of the swallow-tailed part (increase of $n$). No good dielectric data of the $\delta$-process could be obtained in the case of P2 because of the high conductivity and clearing temperature. The $\delta$-process of P6 could be separated from the conductivity by the aid of a double logarithmic plot.

Unfortunately, the polymers could not be oriented in the measuring cell. However, from microscopic observations we know that there is a tendency to a homeotropic orientation. As the absorption intensity depends on the orientation of the molecules[9] we can explain our results as follows: The decrease of $C''$ at the phase transition isotropic—$S_A$ (Figure 4) and the decrease in the liquid crystalline phase with decreasing temperature (Figure 3) are possibly hints to a partly antiparallel orientation of the side chains. For P16 relaxation frequencies of the $\delta$-process could be determined only in the isotropic phase (Figure 4). In the $S_A$ phase this relaxation was completely covered by the conductivity. This result can be explained by the relatively small dipole moment and an additional compensation due to the above mentioned tendency to an antiparallel arrangement.

All detected relaxation frequencies of the polymers and of M9 are presented in Figure 5. For P2 only one relaxation process was observed. Because of the position of measuring points in the Arrhenius-diagram and the high clearing temperature this process was called $\alpha$-relaxation. The relaxation frequencies of the $\alpha$ process depend on the length of the side chains indicating the influence of this part of molecule on this complex motion.[10]

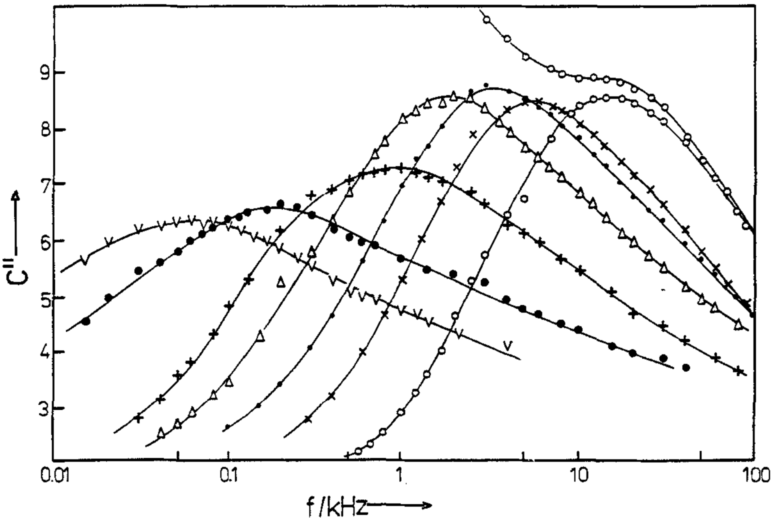


FIGURE 3 $\delta$-Relaxation curves for P9 in the isotropic phase (o, ×, ·, Δ) and $S_A$ phase (+, •, v). For $T$ = 355 K the $C''$ values in $nF$ including the loss caused by the conductivity are shown (upper curve). o: 355 K, ×: 345 K, •: 340 K, Δ: 335 K, +: 330 K, •: 324 K, v: 320 K.

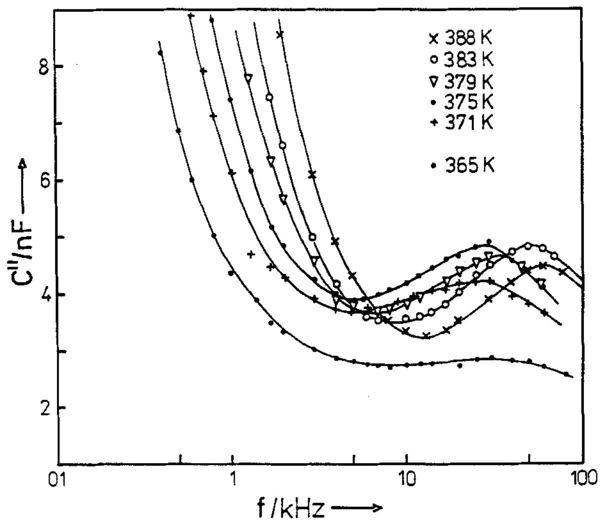


FIGURE 4 The δ-process for P16 in the isotropic phase. In the $S_A$ phase at 365 K the relaxation is completely covered by the conductivity.

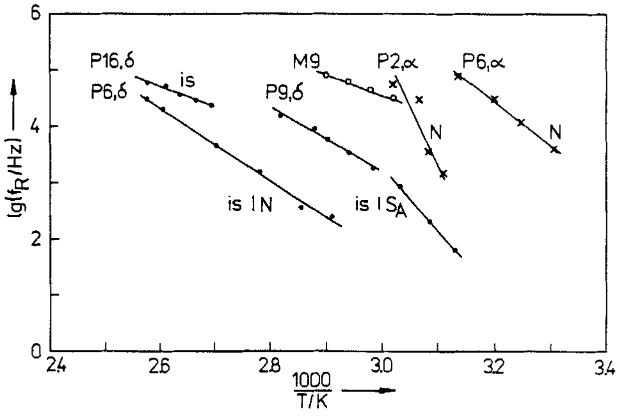


FIGURE 5 Arrhenius-diagram for the investigated polymers and M9 ($S_A$ phase).

At $T^{-1} = 3.05 \times 10^{-3}$ $K^{-1}$ the relaxation frequency of M9 amounts 23 kHz and of P9 0.5 kHz. That means comparable reorientations in polymers require about two decades more time than in monomers.

The experimental data of the polymers can be interpreted by a model of a molecular "zip-fastener."

## Acknowledgment

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