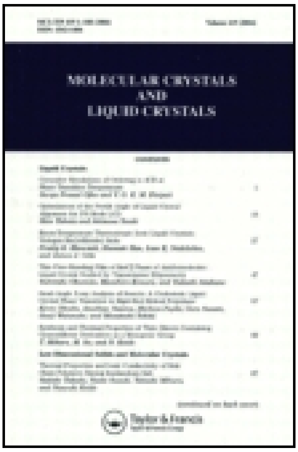

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# Dielectric and Electrooptic Properties of a Switchable Ferroelectric Liquid Crystalline Side Chain Polymer

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# Dielectric and Electrooptic Properties of a Switchable Ferroelectric Liquid Crystalline Side Chain Polymer

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For a switchable ferroelectric liquid crystalline side chain polymer the dielectric spectra for both SmC* and SmA* phases as well as the temperature dependences of the relaxation frequencies are obtained. Only soft and molecular modes take place in the interval $10^1$ to $10^7$ Hz. No Goldstone mode has been observed. The low frequency ($\sim 10^2$ Hz) of the soft mode in polymeric ferroelectric liquid crystals is discussed in terms of a sharp rise of rotational viscosity with increasing molecular weight of FLC molecules. Results of the electrooptical measurements (tilt angle and response time) are also reported. The optical tilt angle varies from zero up to about 25° in the SmC* phase. The switching time increases with decreasing temperature from a minimum of about one millisecond. A short description of the chemical synthesis is also given.

*Keywords: dielectric spectroscopy, electrooptic properties, synthesis, ferroelectric liquid crystalline side chain polymer, viscosity*

## INTRODUCTION

Thermotropic liquid crystals, discovered more than a century ago,[1] are still very actual materials in research and application. Two of their major developments in

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the recent past have been the realization of liquid crystalline polymers and the discovery of smectic phases exhibiting a nonvanishing spontaneous polarization, like the ferroelectric smectic C* phase. It was a promising step when Shibaev *et al.*[2] in 1984 combined both of these properties in the first ferroelectric liquid crystalline side chain polymer (FLCP). The strong interest in these new materials is based on the ferroelectric properties in the mesophase and the possibility of freezing their alignment into the glassy state.

It is known, that ferroelectric liquid crystals (FLC's)[3] based on chiral tilted smectic phases (SmC*, SmI* . . .) have two specific modes for motions of the director, the soft mode and the Goldstone mode.[4–12] They are monitored by the dielectric spectroscopy as responses with different characteristic frequencies and intensities. The soft mode is connected with the change of the molecular tilt angle $\Theta_0$. It usually has a characteristic frequency of $10^5$ to $10^6$ Hz for low molar mass liquid crystals. The Goldstone mode describes the motion of the molecular director along a cone surface with the angle $2\Theta_0$. This mode is usually oberved at $10^2$ to $10^3$ Hz for low molar mass liquid crystals. To identify the observed ferroelectric mode the influence of an outer electric DC-field on the dielectric spectrum can be studied. The Goldstone mode can be suppressed by such a DC-field,[4–6,13] whereas no significant influence can be observed on the soft mode relaxation strength,[4] except in the narrow vicinity of the SmC*—SmA transition.[6,14] It is emphasized that two components of the rotational viscosity $\gamma_\Theta$ and $\gamma_\varphi$ are needed for the description of these two ferroelectric processes.[15–18]

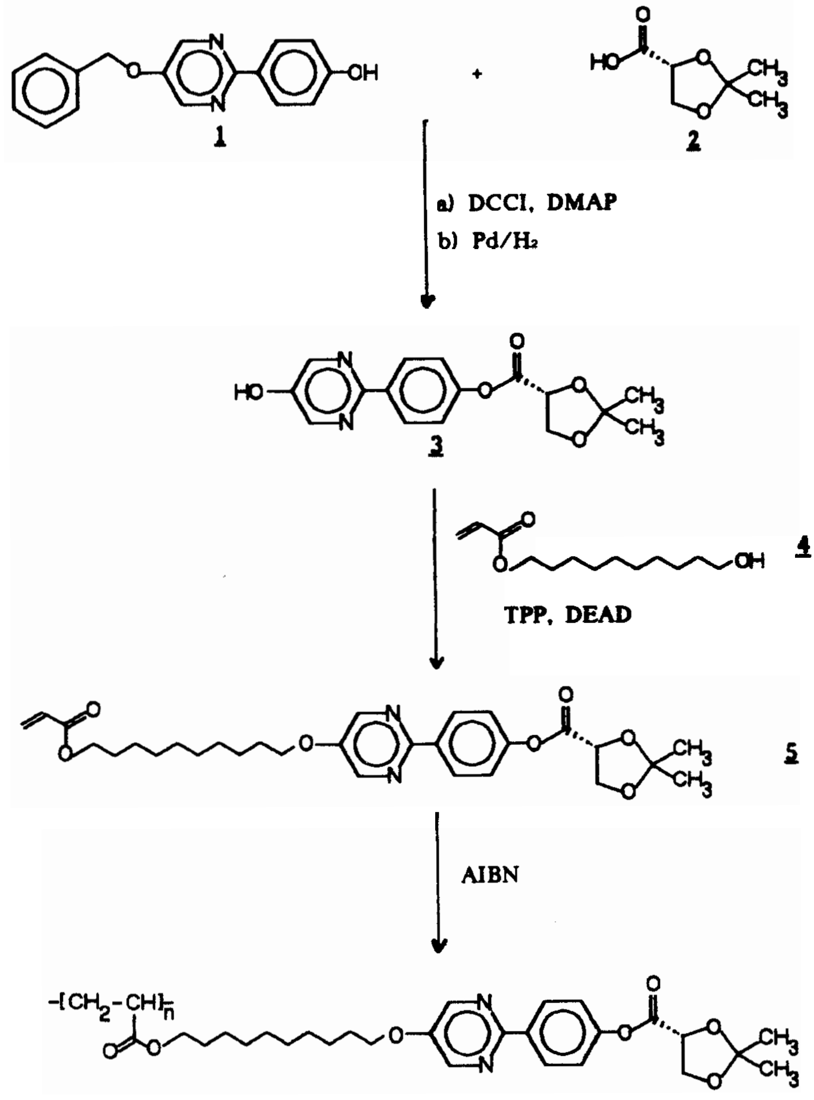
Due to the small value of $\gamma_\varphi$ (which is connected to the Goldstone mode) with respect to $\gamma_\Theta$ (connected to the soft mode) a very fast electrooptical switching of FLC's is possible.[19] The switching time is 50–100 times smaller than in nematic phases at the same driving voltages. This represents the small value of $\gamma_\varphi$, which is about 50 to 100 times less than $\gamma_\Theta$, the equivalent to the nematic rotational viscosity.[16,20]

After the discovery of switchable FLCP's[21,22] it was found that their switching time at comparable electric fields is about $10^3$ times higher than that of FLC's.[19,22] From this fact the question arises: what happens with the two components $\gamma_\Theta$ and $\gamma_\varphi$ of the rotational viscosity, the characteristic relaxation frequencies and the switching times going from low molar mass to polymeric liquid crystals? Are these viscosities and corresponding relaxation processes connected with the motion of separate molecules respectively side chains or are they connected with collective motions of assemblies of molecules or side chains connected via the main chain?

## EXPERIMENTAL

### Synthesis of FLCP PS 291

The polymer was prepared as outlined in the following reaction scheme (Scheme I). Monobenzylated dihydroxyphenylpyrimidine **1** was combined with the chiral dioxolane carboxylic acid **2** by mild esterification using dicyclohexyl carbodiimide (**DCC**) and 4-dimethylaminopyridine (**DMAP**). After deprotection by hydrogenolysis the obtained chiral mesogene **3** was treated with ω-hydroxydecylacrylate **4**



**Polymer PS 291**

SCHEME I Synthetic scheme of PS 291.

in the presence of triphenylphosphine (**TPP**) and diethylazodicarboxylate (**DEAD**) (Mitsunobu reaction) to give the monomer 5.

### (R)-4-[5-(10-acryloyloxydecyloxy)pyrimidine-2-yl]-phenyl-2,2-dimethyl-1,3-dioxolane-4-carboxylate (5)

To a solution of 1.26 g (4 mmol) of 3, 0.91 g (4 mmol) of 4 and 1.05 g (4 mmol) of **TPP** in 50 ml of tetrahydrofuran (**THF**) a solution of 0.70 g (4 mmol) of **DEAD** in 20 ml of **THF** was added dropwise. After stirring for 12 hours the precipitate was separated. The remaining solution was evaporated and the residue purified by flash chromatography using $CH_2Cl_2$/petrolether mixtures as eluent.

Yield: 700 mg; mp. 83.5–84°C.—$[\alpha]_D^{23} = +6{,}9°$ ($c$ = 1.08, in $CHCl_3$).—$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.3–1.4 (m; 5 $CH_2$), 1.47 (s; Me), 1.48 (quint; $J$ = 7 Hz, $CH_2$), 1.57 (s; Me), 1.67 (quint; $J$ = 7 Hz, $CH_2$), 1.83 (quint; $J$ = 6.5 Hz, $CH_2$), 4.09 (t; $J$ = 6.5 Hz, $CH_2$), 4.15 (t; $J$ = 7 Hz, $CH_2$), 4.33 (dd; $J$ = 9 and 5 Hz, 1 H), 4.39 (dd; $J$ = 9 and 7 Hz, 1 H), 4.85 (dd; $J$ = 7 and 5 Hz, 1 H), 5.81 (dd; $J$ = 10.5 and 1.5 Hz, 1 H), 6.12 (dd; $J$ = 17.5 and 10.5 Hz, 1 H), 6.40 (dd; $J$ = 17.5 and 1.5 Hz, 1 H), 7.21, 8.38 (AA'BB'; $J$ = 8.5 Hz, 4 H), 8.44 (s; 2 H). —MS (235°C): m/e = 526 ($M^+$, 5%), 511/(M-Me, 6), 398 (100), 326 (4), 188 (40).

### Polymerisation. Poly-(R)-10-[4'-(2,2-dimethyl-1,3-dioxolane-4-carbonyloxy)-phenyl-1,3-pyrimidin-2-yl-5-oxy]-decylacrylate (PS 291)

636 mg (1.21 mmol) of monomer 5 were polymerized with 2.0 mg (0.012 mmol) of **AIBN** under nitrogen in 6 ml of dry **THF** at 60°C for 18 hours. Thereafter the polymer was precipitated by adding methanol. For purification the precipitation from concentrated **THF** solution was repeated five times. Yield: 480 mg (75%). $M_W$ = 7600 g/mol, $E = M_W/M_N = 1.38$. The phase sequence is obtained by DSC and polarizing microscopy. The phase identification of the SmC* and SmA phases are obtained by X-ray diffraction:

glass 29°C SmC* 85–88°C SmA 110–115°C I.

Unfortunately the substance is not very stable in the isotropic phase.

### Electrooptical Measurements

The electrooptical measurements were performed in ITO-coated cells (4 μm thickness, 0.16 $cm^2$ active area) with parallel rubbed polyimide alignment layers. The cells were filled by capillary action. To improve the orientation an electrical field treatment was used. The cells were thermostated during the measurement in a Mettler hot stage FP 80.

Attempts to measure the spontaneous polarization[23–27] failed due to a strong polarization process of charged impurities in the material. The temperature and field strength dependent measurements of the tilt angle and the switching time were performed using a polarizing microscope. The tilt angle was determined from the angle of rotation of the microscope stage between the two extinction positions of the switched FLCP between crossed polarizers. We used field strengths up to ±22.5 V/μm to be in the saturation range. As time between successive tilt angle measurement we took 3 minutes. Additionally to these measurements we determined the tilt angle from the layer spacing obtained by x-ray diffraction measurements (modified Stoe Stadi 2 powder diffraction system).

The optical rise times were obtained using a photodiode by applying fields up to ±20 V/μm. The optical rise time is defined as the 10–90% response time of the FLCP. Below 35°C we applied DC voltage up to 12 h to achieve complete switching.

### Dielectric Spectroscopy

For dielectric measurements gold coated electrodes and a cell thickness of 11 ± 1 μm were used. To obtain planar orientation (bookshelf geometry) the cell, filled by capillary action in the isotropic phase, was slowly cooled (−3K/h) into the SmA phase within a magnetic field of 1.2T. The alignment was checked using a polarizing microscope. Once aligned in bookshelf geometry the material kept its alignment without any magnetic field. So the field could be switched off, not to suppress the Goldstone mode.[13] The dielectric spectra were obtained using the HP4192A impedance analyzer controlled by an Atari Mega ST2 computer. The temperature was controlled by an oil bath and kept constant better than ±0.02 K.

## RESULTS AND DISCUSSION

### Tilt Angle

In Figure 1 the field strength dependence of the optical tilt angle (Θ) of PS 291 is given. An increase of the tilt angle with increasing voltage is evident. To switch the mesogenes into the extreme positions on the ferroelectric cone field strengths of 12 V/μm up to 20 V/μm are necessary (saturation). The critical field strength for total switching increases with decreasing temperature. We interpret the weak increase of Θ at higher fields as the electroclinic effect.

The temperature dependence of Θ is given in Figures 2a–c. At lower field strengths (Figure 2a) appears a minimum in the optical tilt angle. This may be due to a noncomplete switching of the mesogenes on the cone, because these data are obtained using a switching frequency of 0.1 Hz. The minimum becomes weaker and shifts to lower temperatures with increasing voltage. Figure 2b shows the data obtained for higher field strengths after sufficiently long time to have an equilibrium

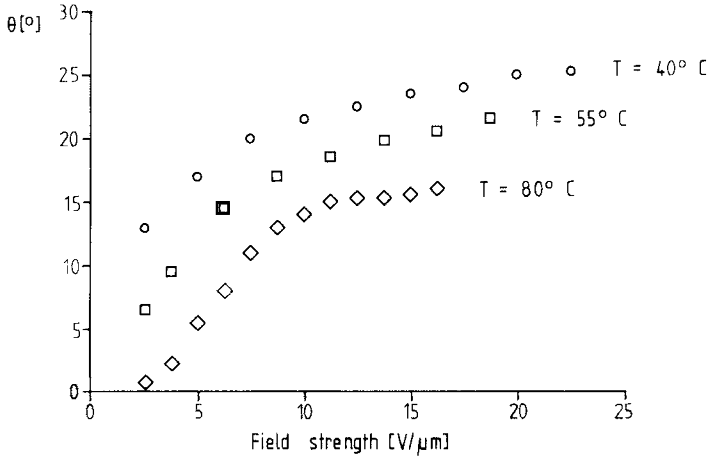


FIGURE 1 Optical determined tilt angle versus field strength (PS 291). The critical field strength for total switching increases with decreasing temperature.

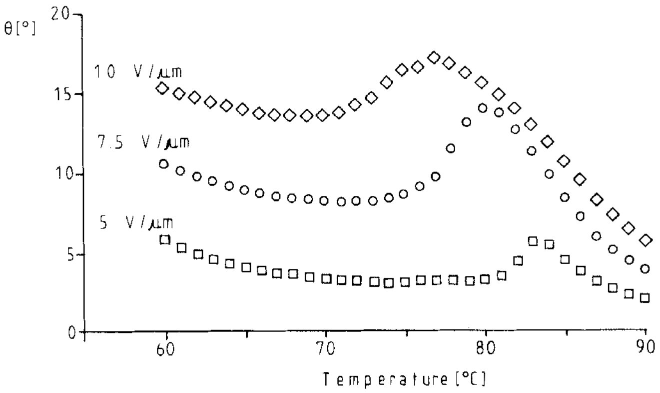


FIGURE 2a Optical determined tilt angle versus temperature at different field strengths (PS 291). The minima are due to imperfect switching.

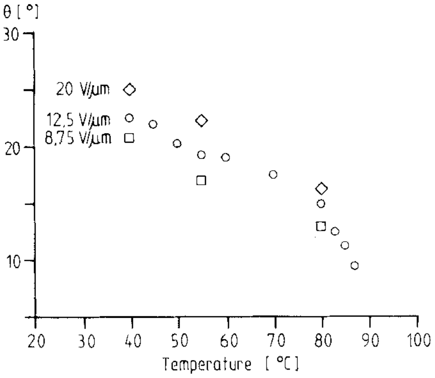


FIGURE 2b Optical determined tilt angle of PS 291 versus temperature at different field strengths.

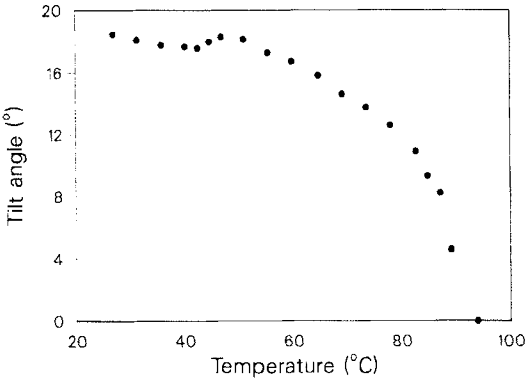


FIGURE 2c Molecular tilt angle of PS 291 obtained by x-ray diffraction.

state, this means for nearly total switching. These data agree qualitatively with the behaviour known from low molar mass FLC's. Measurements at even higher field strengths than 20 V/μm would lead to exact values of the optical tilt angle also at lower temperatures but were not possible due to decomposition and electrical breakdowns. Figure 2c shows the molecular tilt angle obtained by x-ray measurements. Here the temperature dependence agrees well with the expected behaviour. The absolute values of $\Theta$ are smaller than those obtained by optical methods. This is in accordance with the zig-zag model of the SmC phase.[28]

## Response Time

A plot of the response time of PS 291 versus temperature is shown in Figure 3a. The switching time increases with decreasing temperature from about one millisecond up to hours. This corresponds with the increasing viscosity of the material. At the glass transition the switching time approaches infinity, this means in the glassy state no switching is possible any more. Figure 3b shows the field strength dependence of the switching time at 55°C. Higher field strengths generally accelerate the switching process. Saturation seemed to be at fields higher than 15 V/μm.

## Dielectric Spectroscopy

In Figure 4 typical curves of the real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ parts of the dielectric constant of PS 291 are presented for some temperatures near the SmA-SmC* transition. They show a distinct relaxation process with a characteristic frequency of about $10^2$ Hz (maximum of $\varepsilon''(\omega)$ curves). The influence of the cable inductivities, the connection resistivities and of the dc-conductivity of the sample are corrected.

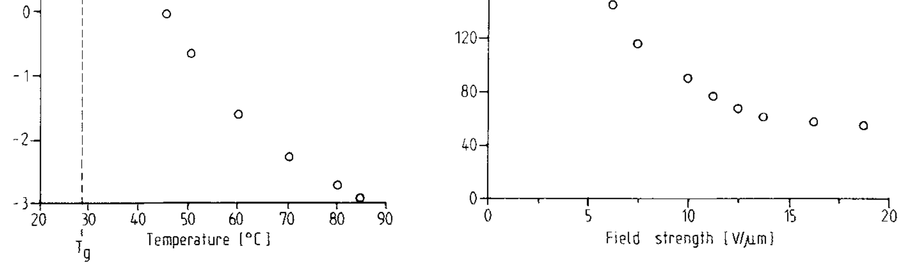


FIGURE 3 (a) Switching time of PS 291 versus temperature ($E$ = 13 V/μm). The switching time approaches infinity at the glass transition. (b) Switching time versus field strength at 55°C. Saturation seemed to be at about 15 V/μm.

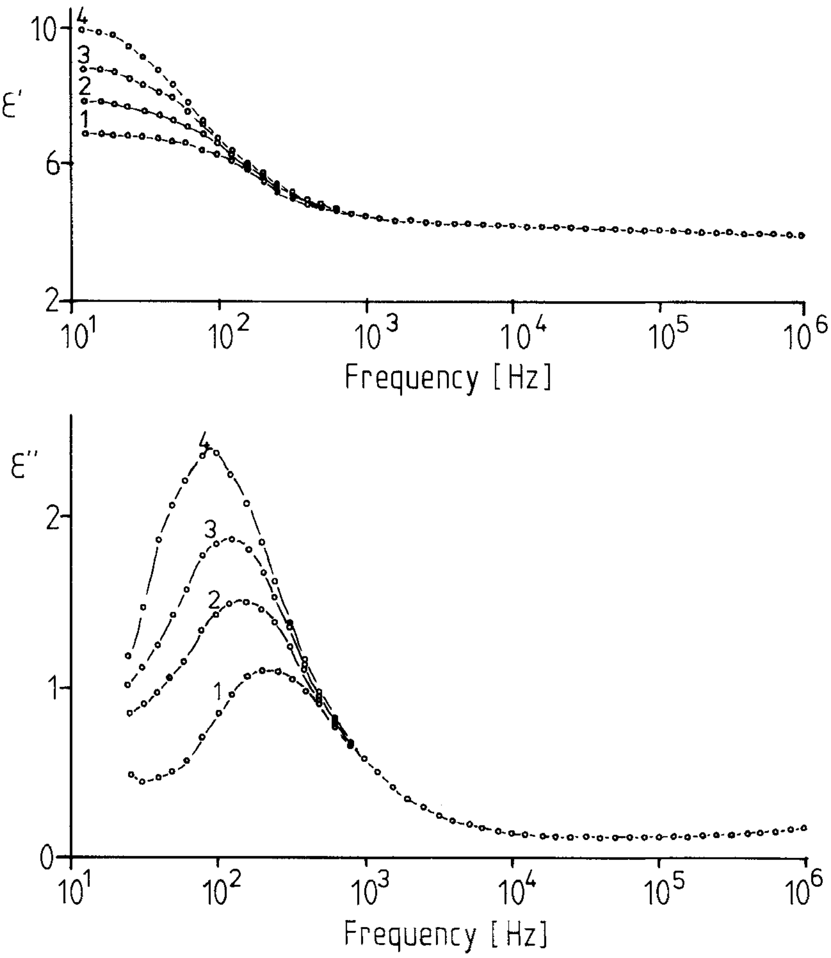


FIGURE 4 Dielectric spectra (real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric constant) of PS 291 at different temperatures in the SmA phase. The temperatures are: 1) 88.6°C, 2) 87.7°C, 3) 87.0°C and 4) 86.0°C.

Another relaxation process (Figure 5) can be observed at lower temperatures and higher frequencies ($10^3$ to $10^7$ Hz). It has a rather small intensity (Figure 8). We consider this mode as a combined molecular relaxation process involving the mesogens movement around its long axis ($\alpha$-relaxation).[10,29] The $\delta$-process (movements around the mesogen's short axis) cannot be observed due to the high quality of alignment and the small component of the dipole moment parallel to the long axis of the mesogene.

Taking into account the good switchability of polymer PS 291 one could suppose, that the low frequency process (Figure 4) is a Goldstone mode. In this case it should be able to suppress this mode by an external dc electric field.[4–6,13,30,31] Results of this experiment are shown in Figure 6. No suppression of this mode

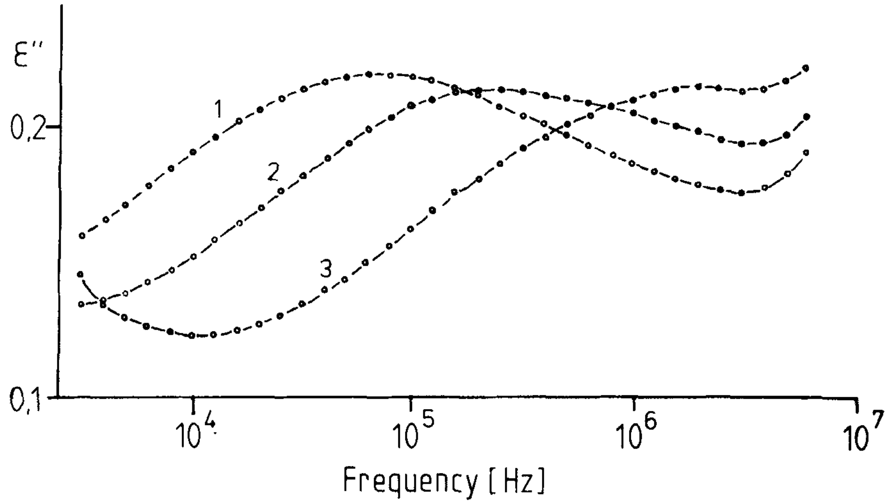


FIGURE 5 Molecular mode of PS 291 at lower temperatures. The temperatures are: 1) 56.5°C, 2) 61.6°C and 3) 70.1°C.

could be found, neither near the transition SmA-SmC*, nor at lower temperatures within the SmC* phase.

The temperature dependence of the dielectric strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ (Figure 7) reveals a very distinct peak at the transition point $T_{CA}$. This is characteristic for the soft mode behaviour.[4-8,15,32] $\Delta\varepsilon$ was determined by fitting a Cole-Cole function to the measured values. In the same figure the $\Delta\varepsilon$ data of the molecular mode are also given. At temperatures above 78°C the spectrum is dominated by the soft mode. The frequency of the weak molecular mode approaches the edge of the investigated frequency range (Figure 8). The temperature dependence of the soft mode frequency $\nu_S$ in the interval 82–110°C is also similar to the soft mode behaviour of low molar mass FLC's (Figures 8 and 9a). The only difference is, that usually the soft mode is observed in a more narrow interval around the transition temperature.[4,7-10,33,34] The broad temperature range of the soft mode of FLCP's was also observed by Vallerien *et al.*[30,35]

The experimental data $\nu_S$, $1/\Delta\varepsilon$ and the product $\nu_S\,\Delta\varepsilon$ as a function of temperature are presented in Figure 9 to compare them to the theoretical predictions for the soft mode parameters.[32] We are not able to derive from the slopes of the $1/\Delta\varepsilon$ curve whether the observed phase transition is first or second order as it is possible for single component FLC's.[6,32] But the temperature dependence of the product $\nu_S\,\Delta\varepsilon$:

$$\nu_S\Delta\varepsilon = \varepsilon^2 C^2/2\pi \cdot 1/\gamma_\Theta \qquad (1)$$

is very similar to that of the low molar mass FLC.[32] In formula (1) $\gamma_\Theta$ is the rotational viscosity which belongs to the soft mode, $C$ the temperature independent coefficient of the piezoelectric bilinear coupling and $\Delta\varepsilon$ represents the dielectric strength of the polarization mode in the SmA* phase. Whereas the temperature dependences

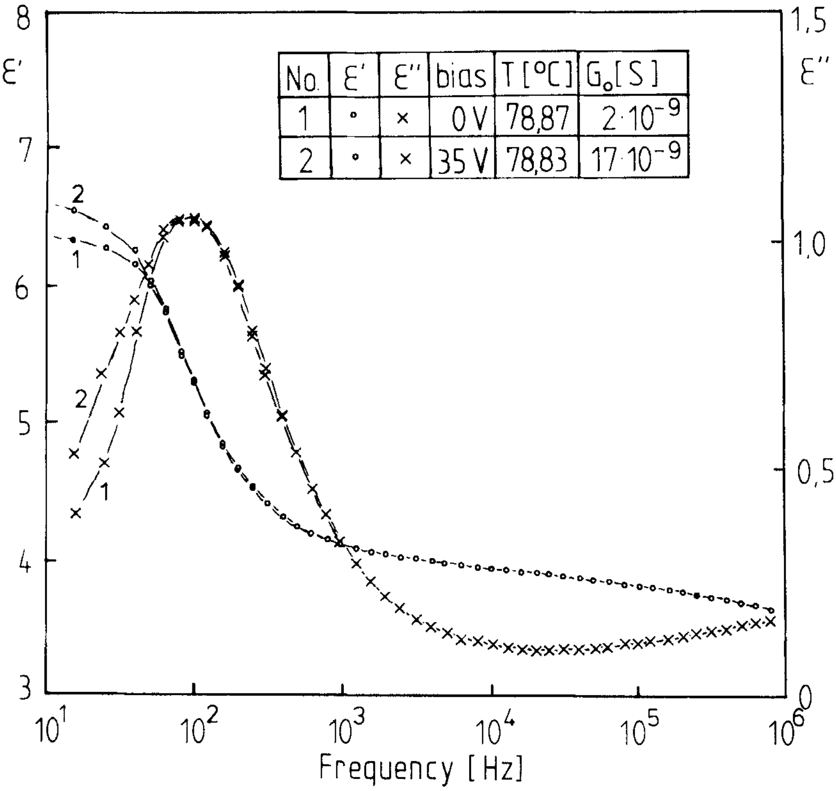


FIGURE 6 Influence of bias field on the dielectric response in the SmC* phase (PS 291). The observed mode cannot be suppressed by an outer electrical field.

of $\Delta\varepsilon$ and $\nu_S$ have some anomalies below 82°C, the product $\nu_S\Delta\varepsilon$ shows expected behaviour, according to Arrhenius's law. As this product represents the inverse rotational viscosity $\gamma_\Theta$ it shows not only a very distinct increase with decreasing temperature, but also the anomaly connected with the critical behaviour of $\gamma_\Theta$ near the transition temperature $T_{CA}$ observed[32] for low molar mass FLC's. Due to the fact that this polymer has a distribution of molecular weight, the investigated parameters do not show a distinct change at the broadened phase transitions like those observed for single components with sharp transitions.[32] Nevertheless all these parameters reproduce typical soft mode behaviour.

The small value of the soft mode relaxation frequency (~80 Hz at $T_{CA}$) of FLCP PS 291 shall be discussed in comparison with low molar mass FLC's ($10^4$–$10^5$ Hz). We suppose that the soft mode is a specific "collective" mode of motion. It can be described as a motion of an assembly of side-group chiral mesogens tied with the main chain. Consequently, the characteristic relaxation frequency $\nu_S$ should not only be connected to the type of the molecule but also to the effective size of the assembly or in a rough approximation to the molecular weight of the polymeric liquid crystal. In Table I we present some published results on relaxation frequencies

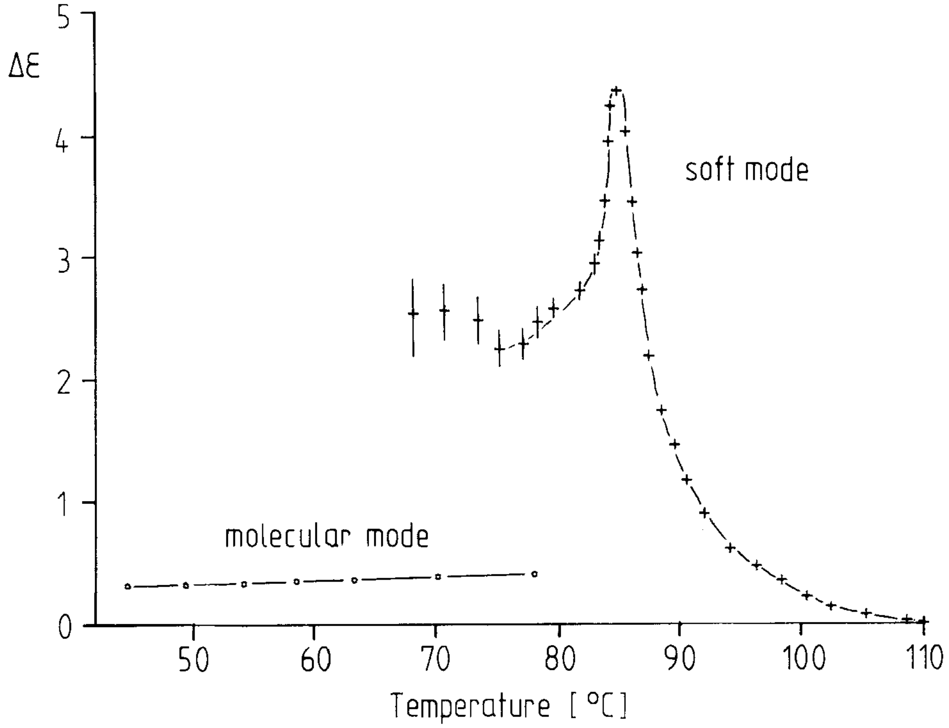


FIGURE 7 Temperature dependence of the dielectric strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ of the soft mode (+) and of the molecular mode (○)(PS 291).

$\nu_S$ of the soft mode for different FLC systems. The data are taken at the transition temperatures $T_{CA}$ or at $T_{IC}$ and $T_{IA}$ if there is no SmC*-SmA transition.

Figure 10 shows the correlation between the soft mode relaxation frequency $\nu_S$ and the molar mass: $\nu_S$ decreases drastically with increasing molecular weight. If this behaviour can be extrapolated within some interval of molar masses we can predict the soft mode characteristic frequency of the polymer PAC-1B[35] to be $\nu_S \sim 20$ Hz at the transition temperature $T_{CA}$. Therefore the authors of paper 35 could not clearly identify the dielectric response of this substance. At such low frequencies the conductivity of their material has covered all processes. Nevertheless it has been shown[36] that polymers with strongly higher degree of polymerisation are still switchable. So at very high molar masses the characteristic frequency of the soft mode should show a weaker dependence on the molar mass. Moreover $\nu_S$ could depend strongly on the mutual concentrations of chiral and achiral components in the mixtures as well as on the transition temperature $T_{CA}$. The complexity of the dielectric spectra, published in Reference 30 for combined side group - main chain FLCP's could be connected to the fact, that these materials represent a special kind of "intrinsic" FLC mixture.

A very slow relaxation of the pyroelectric response of FLCP's after heating with short thermal laser pulses has been observed.[2,37] The decay time of the pyroelectric response of these materials increased critically from 0.1 ms and 1 ms near the

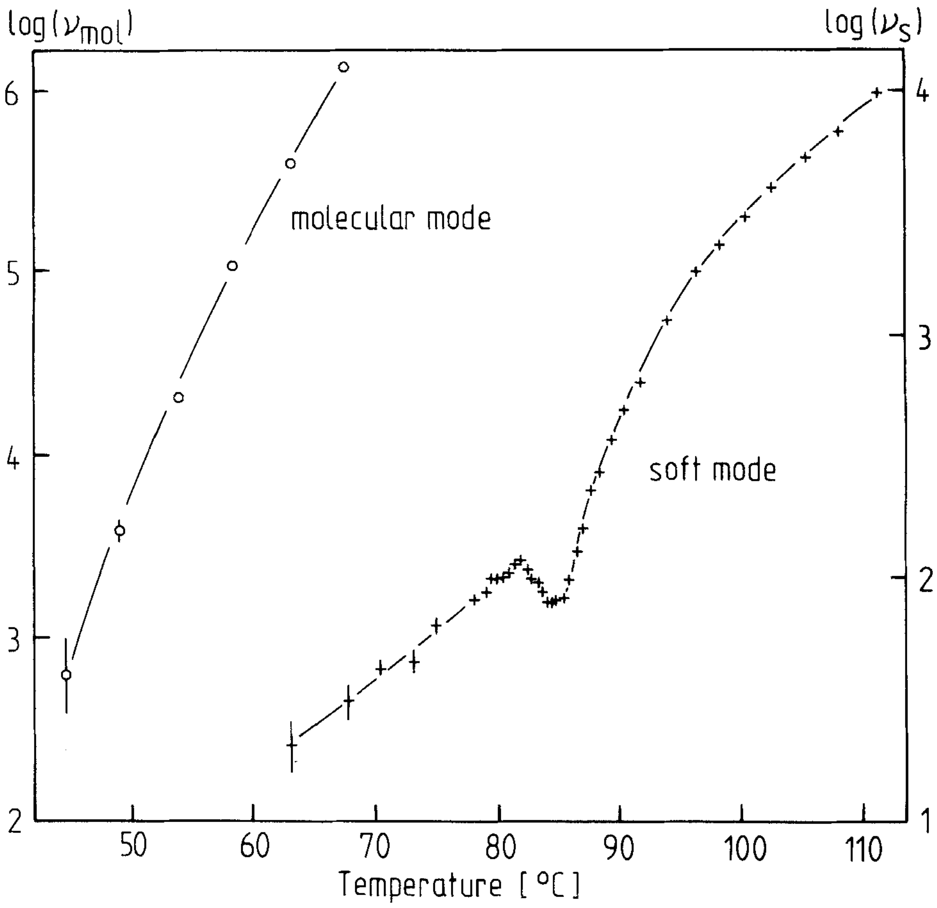


FIGURE 8 Temperature dependence of the relaxation frequency of soft (+) and molecular (○) modes (PS 291).

transition SmC*-SmA*. This corresponds to a relaxation frequency at $T_{CA}$ of less than 160 Hz. We consider that the authors of the papers 2 and 37 have dealt with a soft mode.

Let us discuss the Goldstone mode in polymeric FLC's. The rotational viscosity $\gamma_\varphi$ determines the electrooptical switching time $\tau_{sw}$ of a surface stabilized ferroelectric liquid crystal (SSFLC) according to the relationship (2)[17,38-40].

$$\tau_{sw} \sim \gamma_\varphi / P_S E \tag{2}$$

$P_S$ represents the spontaneous polarization and $E$ the driving electrical field. It is possible to estimate values of $\gamma_\varphi$ for low molar mass and for polymeric FLC's from the switching time $\tau_{sw}$ measured at the same experimental conditions (thickness, driving voltage). The correlation between $\gamma_\varphi$ and the Goldstone mode relaxation frequency $\nu_G$ is given in equation (3)[19,41]:

$$\nu_G^{-1} = \tau_G \sim \gamma_\varphi / K q_0^2 \tag{3}$$

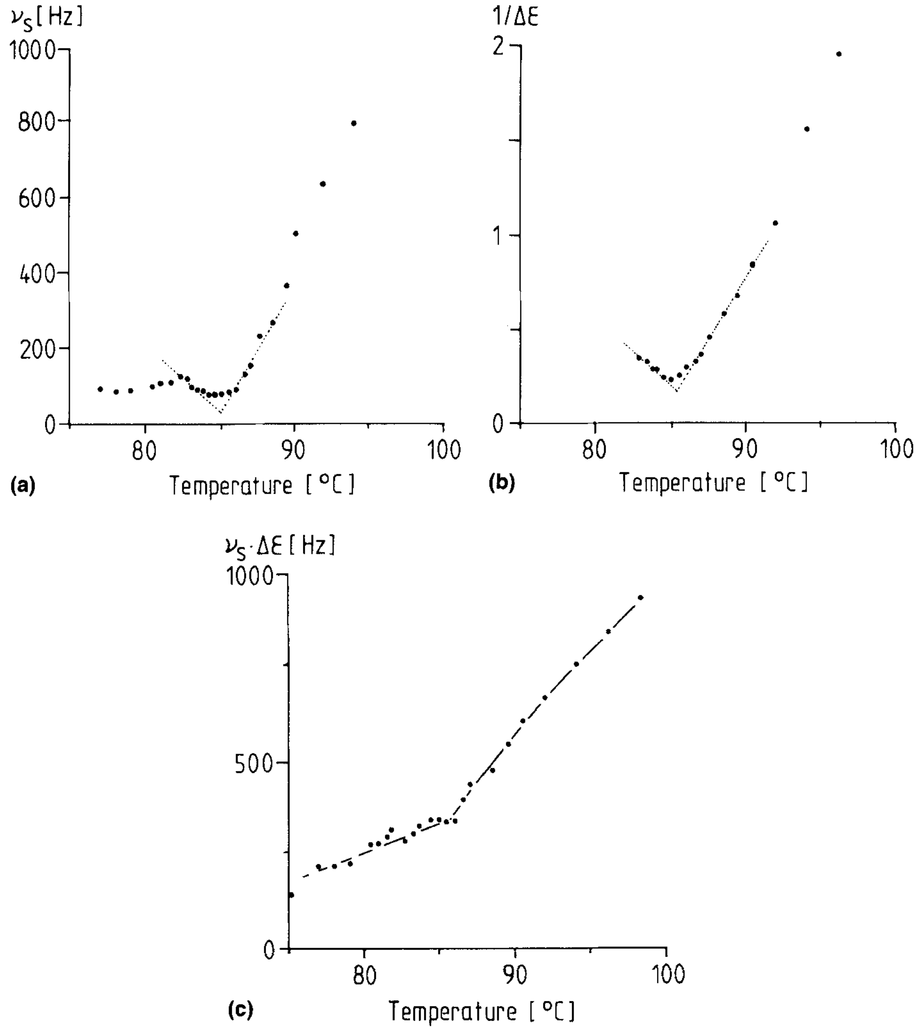


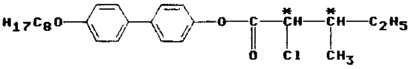
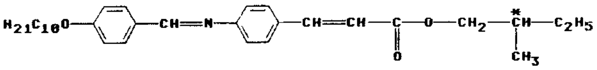
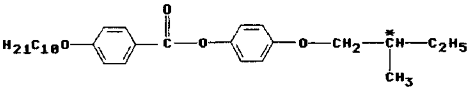
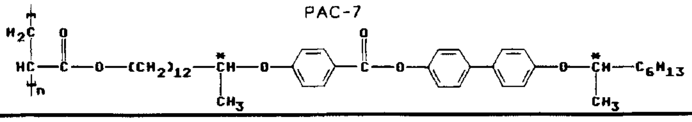
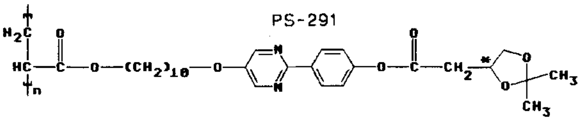
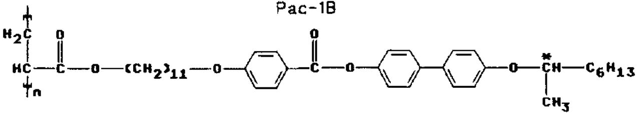
FIGURE 9 Temperature dependence of (a) the soft mode relaxation frequency $\nu_S$, (b) the inverse of the soft mode dielectric response $1/\Delta\varepsilon$, and (c) the product $\nu_S\Delta\varepsilon$ of PS 291.

$K$ is an elastic modulus, $q_0$ the helical wave vector. With this equation the orders of the characteristic relaxation frequencies of low molar mass and polymeric FLC-systems can be evaluated under the assumption that the elastic modulus and the wave vector are approximately the same for low molar mass and polymeric FLC's. The possible characteristic frequency of the Goldstone mode of FLCP's should be very small compared to low molar mass FLC's. It should be expected similar to[27] in the subhertz region for our compound (Table II). The conductivity dominates the dielectric spectrum in this frequency region. Therefore measurements have not been possible below 10 Hz.

The very long relaxation time ($\sim 10^2$ s) of the pyroelectric response after switching

TABLE I

Published soft mode relaxation frequencies of some FLC's at their transition temperatures

| No. | FLC material | $M_W$ [u] | $T_{CA}$ [°C] | $\nu_s$ [kHz] | Ref. |
|---|---|---|---|---|---|
| 1 | 3M2CPOOB  | 431<br>431 | 56.6<br>55 | 15<br>10 | 16<br>7 |
| 2 | DOBAMBC  | 477 | 90 | 50 | 18 |
| 3 | 2MBPDB  | 440 | 48.0 | 90 | 32 |
| 4 | PAC-7  | 2100<br>($S_I$-$S_C$) | 42 | ~1 | 35 |
| 5 | PS-291  | 7600 | 85 | 0.08 | our data |
| 6 | Pac-18  | 15000 | ~142 | our pre-diction: (0.02) | 35 |

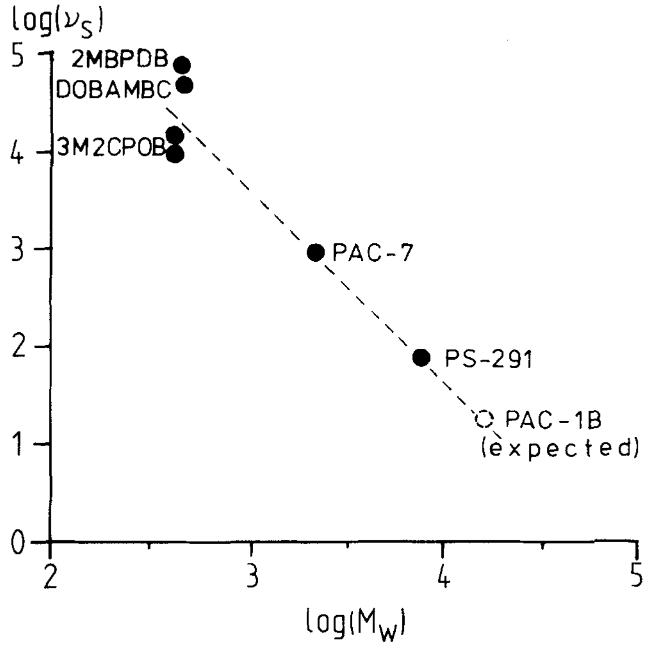


FIGURE 10 Dependence of soft mode relaxation frequency at the transition SmC*-SmA on the molecular weight $M_W$ of ferroelectric liquid crystals (low-mass as well as polymeric). More data about the substances are given in Table I.

TABLE II

Comparison of the characteristic switching times $\tau_{sw}$ and the relaxation frequencies $\nu_G$ of the Goldstone mode for low molar mass and polymeric FLC's

| | Low molar mass FLC | Polymeric FLC |
|---|---|---|
| $\tau_{sw}$ [s] | $10^{-6}$ - $10^{-5}$ [19] | $10^{-3}$ - $10^{-2}$ [21,22] |
| $\gamma_\varphi$ [Poise] | ~0.1 - 1.0 | $10^2$ - $10^3$ |
| $\nu_G$ [Hz] | ~$10^2$ - $10^3$ | 0.1 - 1.0 |

off an external untwisting electric field[42,43] is most probably connected to the Goldstone mode.

The high values and the stronger temperature dependences of the viscosity of FLCP's with respect to low molar mass FLC's strongly influences their electrooptical and dielectric behaviour. Further electrooptical and dielectric measurements of the characteristic relaxation frequencies and the rotational viscosities of specially synthesized sets of FLC's with variable molecular weight (dimers, trimers and so on) should elucidate the problem of connecting these parameters to the molecular structure.

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