Dielectric Studies of a Series of Liquid Crystalline Pyridine Derivates

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Measurements of the temperature and frequency dependence of dielectric constants have been performed for five homologues in the range 100 Hz - 10 MHz. These substances exhibit a negative anisotropy of the dielectric constants and two relaxation regions (rotation of the molecules around the short resp. long axis) in the investigated frequency range. Even in the crystalline state dipolar reorientations are possible which have been interpreted as rotations of the alkoxy group. Changes of the static dielectric constants, relaxation frequencies and transition entropies are discussed as a measure of structural changes passing the several liquid crystalline phases.

Key words: Dielectric constants, Relaxation frequencies, Transition entropies, Tilted smectic phases.

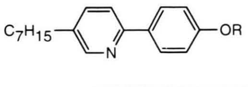
Introduction

For about 15 years the dielectric properties at phase transitions have already been under investigation [1 - 5]. There is no doubt that dielectric measurements are a suitable tool to observe structural changes. Many papers have been published with the aim of systematizing the results and ordering the phase transitions into a scheme. But, till now there is no satisfactory survey regarding the behaviour of relaxation frequencies at phase transitions caused by the variety of polymorphisms.

In this paper we report on dielectric studies and results of calorimetric measurements of a series of liquid crystalline pyridine derivates **Pn** [6] whose phase transition temperatures are listed in Table 1.

Table 1. Abbreviations and phase transition temperatures of **Pn**.

R	Abbr.	Phase sequence (T/°C)
C_4H_9	P4	Cr 54 (S_G 40 S_F 48) S_C 64 N 70 Is
C_5H_{11}	P5	Cr 27 S_G 35 S_F 48 S_C 68 N 69 Is
C_6H_{13}	P6	Cr 34 (S_H 31) S_G 44 S_F 53 S_C 74 N 75 Is
C_7H_{15}	P7	Cr 24 S_H 31 S_G 40 S_F 53 S_C 77 Is
C_8H_{17}	P8	Cr 45 S_G 45.5 S_F 56 S_C 80 Is



Pn

These substances are very interesting as they have a rich polymorphism, low clearing temperatures and good chemical stability. To materials with tilted smectic phases great attention is paid because of their relevance for electro - optic effects and device applications [7]. Dielectric measurements in an extended temperature and frequency range were carried out in order to get information about the static dielectric behavior in several phases and about the rotational possibilities of molecules. As a general rule, in liquid crystals there are two dielectrically observable molecular reorientation processes, which have also been detected in the above substances. A special interest is aimed at the changes of relaxation frequencies at phase transitions because such changes make visible the increasing molecular order coming from the isotropic state via liquid crystalline phases to the crystalline state.

Experimental

The substances **P4** - **P8**, synthesized by the Chisso Corp. [6], have been investigated in the frequency range 100 Hz - 10 MHz using the impedance analyzer HP4192A. The probe is located between the plates of a brass condensor (A = 1 cm^2 , d = 0.02 cm) which has been calibrated with cyclohexane. In the case of those materials, exhibiting the phase sequence Is–$\underline{\text{N}}$–S_C–$\cdots$, the molecular director could be oriented in directions parallel and perpendicular to the measuring

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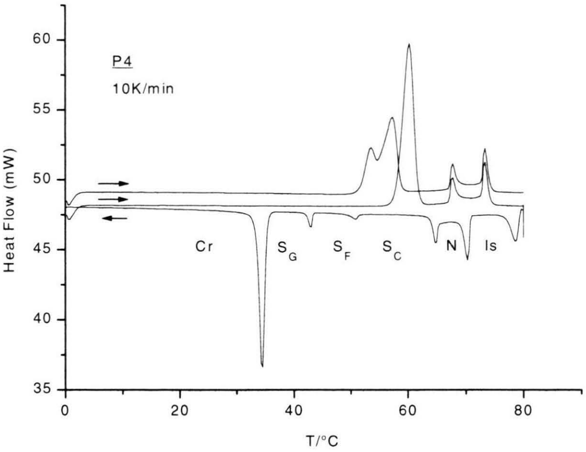


Fig. 1. DSC thermograms for **P4** at a heating and cooling rate of 10 K/min.

field by the aid of a magnetic field of about 0.7 T. Unfortunately, the strength of the magnetic field was not sufficient to orient the molecules in **P7** and **P8** which do not have the nematic phase.

High frequency measurements in the range 1 MHz - 1 GHz (impedance analyzer HP4191) have been done only for **P4**. The obtained results were assumed to be valid for the other pyridines, too. For calorimetric measurements a DSC7 (Perkin Elmer) was used. The phase transition temperatures and entropies have been determined during several heating and cooling runs at different rates.

Results and Discussion

Before discussing the results we should mention that there is a deviation between the phase transition temperatures determined by microscopy and the temperatures detected by dielectric measurements. This deviation amounts about 1K - 2K caused by the non - constant position of the thermocouple and the distance between the place of temperature measurement and the substance during the dielectric measurements. In Table 1 the microscopically determined temperatures are given. The designation of the low temperature smectic phases was taken from [6]. Our microscopic and calorimetric investigations confirmed the given phase sequences. The DSC scans of **P4** are shown in Figure 1. X - ray measurements on oriented samples of **P6** provided on the equator the typical diffuse scattering of the S_F phase [8] with which a clear differentiation from the S_I phase was possible [9].

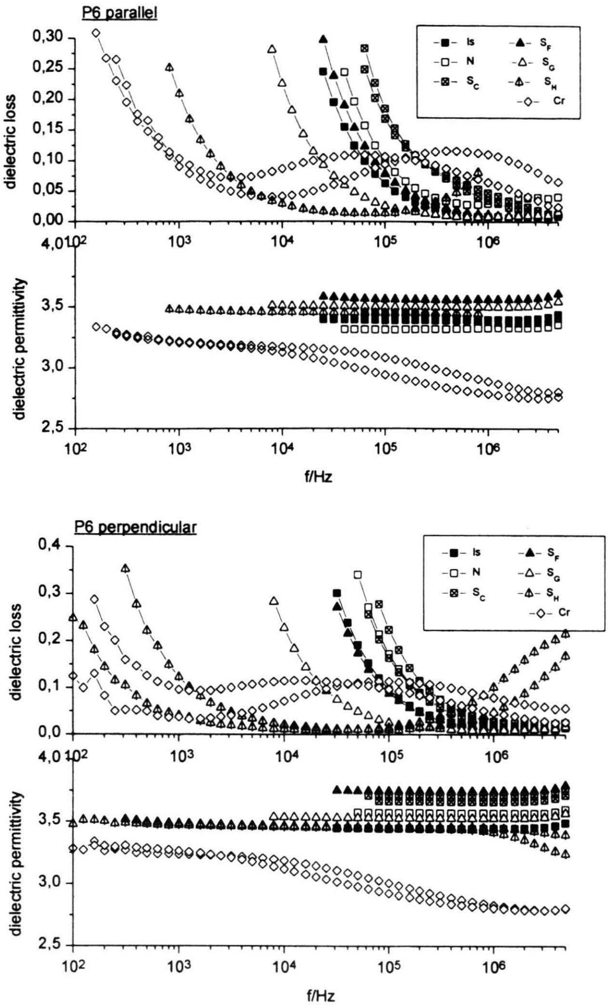


Fig. 2. Experimental curves of dielectric permittivity ε' and dielectric loss ε'' of **P6** for both orientations (parallel, perpendicular).

As an example some experimental curves of the parallel and perpendicular component of the dielectric permittivity and loss of **P6** are shown in Figure 2. The data have been measured with decreasing temperature. At the first glance one realizes a dielectric absorption in both directions in the crystalline state, and in the high temperature phases the markable increase of the measured loss with decreasing frequency. This is due to the contribution of conductivity to the overall loss, which makes it difficult to separate a relaxation due to dipolar rotation.

In order to extract the static dielectric constants ε_0, the measured dispersion curves have been fitted

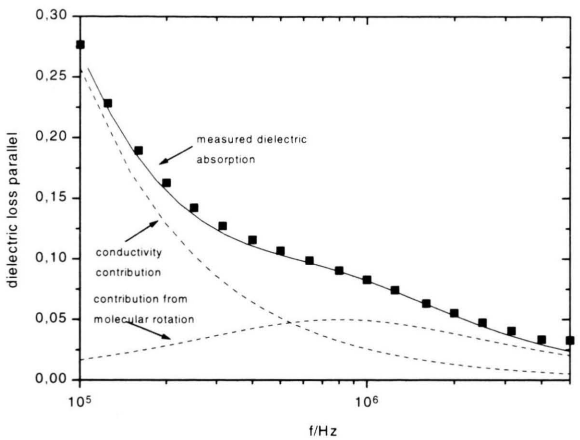


Fig. 3. Frequency dependence of the measured dielectric loss (parallel) at 62.8 °C for **P4**; fit parameters: $\varepsilon_0 - \varepsilon_\infty = 0.12$, $f_R = 8.03 \cdot 10^5$ Hz, $h = 0.9$, $A = 2.6 \cdot 10^4$ Hz.

to the COLE - COLE - equation (1) [10] or, in the case of absence of any dispersion, the measured ε' at 100kHz has been taken as static dielectric constant. Relaxation frequencies have been obtained by fitting the absorption curves according to a modified COLE - COLE - equation (2):

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

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

f, f_R - frequency, relaxation frequency; ε', ε''- dielectric permittivity, dielectric loss; h - Cole-Cole parameter (= 1 for ideal relaxations of the Debye type); ε_0 - static dielectric constant (low frequency limit); ε_∞ - static dielctric constant (high frequency limit).

The second term of (2), Af^{-1}, represents the conductivity contribution with the fitting parameter A. The separation of the dielectric loss due to dipolar reorientation from the measured total loss is illustrated in Figure 3.

The Static Dielectric Permittivity

Figures 4 a - e provides an overview of the temperature dependence of static dielectric constants for all substances. As already mentioned, orientation of the molecular director and measurements of the parallel and perpendicular component of ε was not possible for **P7** and **P8** because of the lacking nematic phase. Two dielectric relaxation mechanisms have been detected in the available frequency range, and that is why there are three quasi-static dielectric constants: ε_{01} (the low frequency limit)- after finishing the low frequency relaxation, ε_{02} - after finishing the high frequency process and before beginning the low frequency process, ε_{03} (the high frequency limit)- before beginning the high frequency process. A theoretical dispersion curve with the above mentioned three quasi-static dielectric constants is depicted in Figure 5.

Because of the dipole moments of the pyridine and the OR-group, acting mainly in perpendicular direction, one observes the expected negative anisotropy of dielectric constants ($\varepsilon_{0\|}$ - $\varepsilon_{0\perp}$) in **P4** - **P8**. At the phase transition N/S$_C$ there is a peculiarity which can be clearly realized in **P4**, the substance with the broadest nematic range: the perpendicular component of ε_{01} as well as the parallel component increase, although one would expect a decrease of $\varepsilon_{0\|}$ and an increase of $\varepsilon_{0\perp}$ due to the tilting of molecules. We are not able to explain these findings since we do not know whether the smectic layers or the molecules themselves are tilted with respect to the magnetic field. But it highlights an often neglected fact. Tilted phases are not uniaxial systems, and it is not sufficient to describe their anisotropic properties with two components $X_\|$ and $X_\perp$. A third one is needed. Only few attempts have been done to estimate three components of ε [11] because it requires special measuring geometries and orientations. At the transition S$_C$/S$_F$ the static dielectric constants change only little: with decreasing temperature $\varepsilon_{0\|}$ decreases and $\varepsilon_{0\perp}$ increases, which can be explained by the increase of the tilt angle. Unfortunately, $\varepsilon_{01\|}$ has been evaluated only till the S$_F$ - phase. With falling temperature the first relaxation process disappears from the available "frequency window" and is completely hidden by the conductivity (see Figure 2). Therefore we have to discuss $\varepsilon_{0\perp}$ and ε_{02}. At the transition S$_F$/S$_G$, $\varepsilon_{0\perp}$ markably drops by about 5% (**P4, P6, P7**), respectively by about 10% (**P8**). This indicates that the dipolar reorientations in S$_G$ are not as free as in the previous phases (S$_F$, S$_C$, N) because of the steplike increase of the molecular order. Substance **P5** seems to be an exception since there is no sharp drop at this transition. The comparison of the

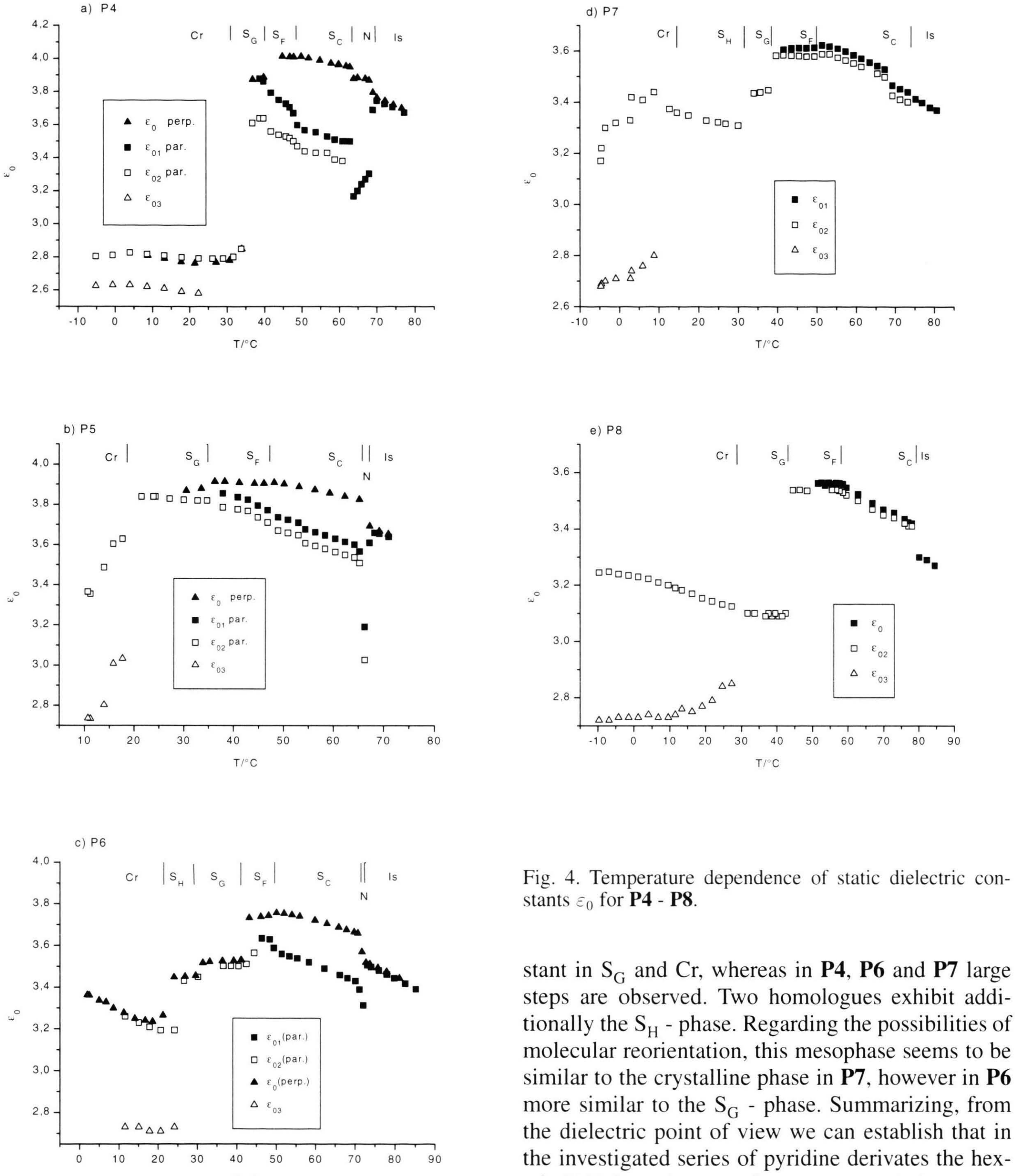


Fig. 4. Temperature dependence of static dielectric constants ε_0 for **P4** - **P8**.

temperature dependence of ε_0 approaching the crystalline phase provides a sophisticated picture. The temperatures of crystallization have been estimated from the calorimetric measurements. In the case of **P8** the static dielectric constants remain nearly constant in S_G and Cr, whereas in **P4**, **P6** and **P7** large steps are observed. Two homologues exhibit additionally the S_H - phase. Regarding the possibilities of molecular reorientation, this mesophase seems to be similar to the crystalline phase in **P7**, however in **P6** more similar to the S_G - phase. Summarizing, from the dielectric point of view we can establish that in the investigated series of pyridine derivates the hexatic [12] S_F - phase can be regarded as belonging to the high temperature phases and the S_G - phase takes a position in between the solid - and liquid like phases. In the first homologues **P4** and **P5**, S_G tends towards the latter, whereas in the higher homologues **P6**, **P7** and **P8** S_G tends towards the former ones.

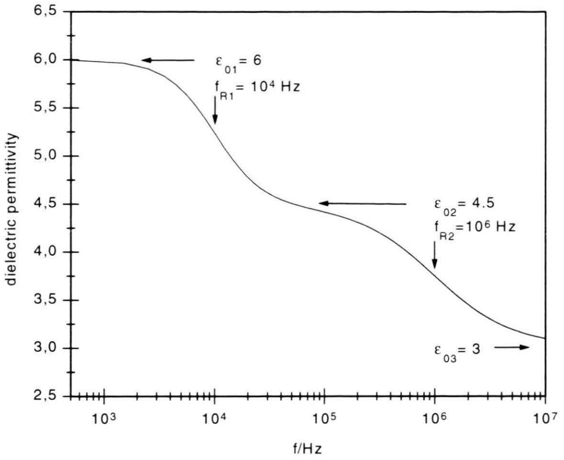


Fig. 5. Theoretical dispersion curve with two relaxation ranges illustrating the quasi-static dielectric constants ε_{01}, ε_{02} and ε_{03}.

The Dynamic Dielectric Behavior

By fitting the measured absorption curves according to (2), the frequencies of maximum dielectric loss (f_R) have been obtained. The temperature dependence of relaxation frequencies is given in Figure 6. As already mentioned, the investigated pyridine derivatives exhibit two relaxation processes in the available frequency range. The low frequency process $\underline{1}$ can be properly described by a Debye - mechanism (h = 1) and is related to the rotation of molecules around their short axis. This molecular motion is indicated by the longitudinal dipole moment which is quite small in the pyridines and causes a small dielectric increment $\Delta_1 = \varepsilon_{01} - \varepsilon_{02}$.

Because of the already mentioned reasons and because of the small increment of about 0.02 (**P8**) - 0.15 (**P4**), the relaxation frequencies of the first relaxation could only be determined with decreasing temperature till the beginnning of the S_F-phase. That is why no information about the f_R at the transition into the low temperature phases could be obtained. Nevertheless, one can discuss changes of f_R at the transitions N/S_C and S_C/S_F (see Table 2). As a measure, the quotient of the relaxation frequencies extrapolated to the transition temperature was calculated. Index 1 designates the high temperature phase and 2 designates the following low temperature phase.

A second physical property, the phase transition entropy ΔS, which characterizes structural changes at phase transitions, is considered. The data show that transitions characterized by large ΔS values exhibit large p values, too. The markable decrease of f_R at the N/S_C transition is a surprising result. Mostly, there is only a change of the activation energy at this transition, however no discontinuous decrease [13]. In **P4** and **P5** this can be explained by the very narrow nematic range (1 - 6 K) and the large influence of pretransition phenomena of the isotropic phase. In contrast to that, very small changes of the mobility concerning rotations around the short axis have been noticed at the transition S_C/S_F, at which the arrangement of molecules within the layers changes from disordered to pseudohexagonal and the long range bond orientational order of the hexatic S_F arises. This is in agreement with the conlusion drawn from the static dielectric behavior, namely the liquid like character of the S_F - phase in **P4** - **P8**.

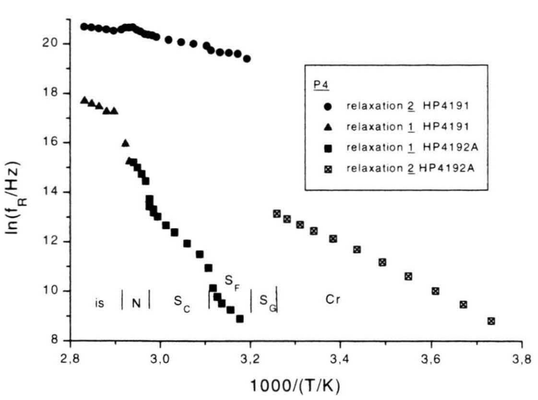
Table 2. Quotients of relaxation frequencies of reorientation around short axis and phase transition entropies from calorimetric measurements.

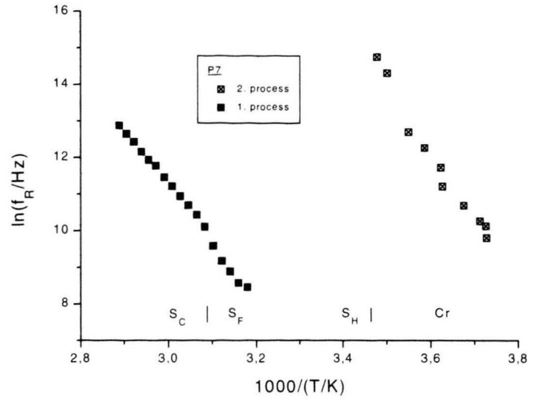
	N/S_C		S_C/S_F	
	$p = f_{R1}/f_{R2}$	ΔS/(J/molK)	$p = f_{R1}/f_{R2}$	ΔS/(J/molK)
P4	2.3	3.4	2	1.3
P5	5	18	1	1.1
P6	–	–	1.6	1.2
P7	–	–	1.5	0.8
P8	–	–	1.2	1.2

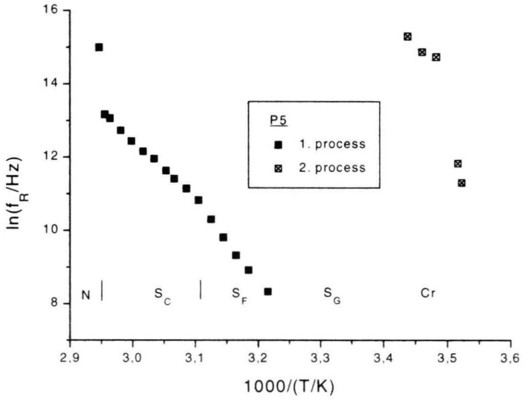
Former dielectric measurements at the transition into S_F or S_I [1,4] showed the sharp drop of f_R with $p = 11$ (S_A/S_F) and $p = 15$ (S_C/S_I). In these cases the S_F and S_I phases seem to have a more solid like character than a hexatic one. Obviously there are significantly different S_F phases. Although we could not determine p-values in S_G, from the comparably large transition entropies of the transition S_F/S_G (2 - 3 J/molK) we expect larger changes of f_R than at the transition S_C/S_F.

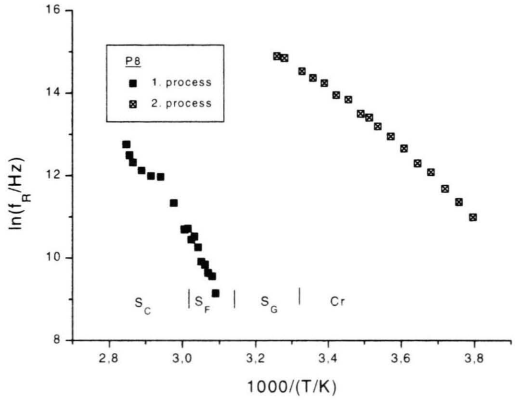
In the substances **P4** - **P8** a second relaxation $\underline{2}$ has been detected in the crystalline state. The absorption curves are broadened compared with those of the first relaxation and have a significantly larger increment of about 0.5. An example is given in Figure 7. This is an unexpected result, since generally the relaxation of the transversal dipole moment is frozen in the crystalline phase. Because of the unequivocal peaks of crystallization, it can be excluded that in this temperature range there is a supercooled smectic phase or a second metastable crystalline phase.

In order to get more information about the second relaxation in the liquid crystalline phases of **P4**,









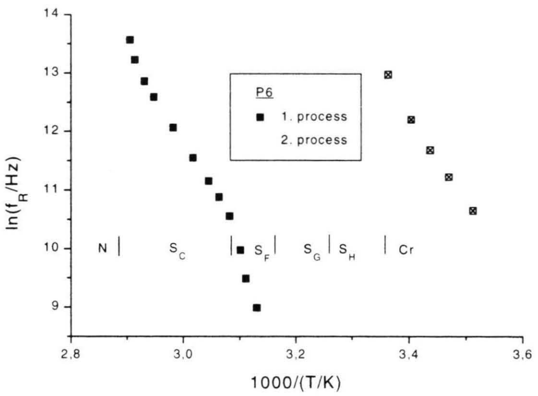


Fig. 6. Temperature dependence of relaxation frequencies (Arrhenius plots).

measurements at higher frequencies (1 MHz - 1 GHz) have been carried out using the impedance analyzer HP4191. More detailed information about the technique is given in [14]. In Fig. 8 the broadened dispersion and absorption curves are depicted, the temperature dependence of which is very small. In the isotropic phase the data have been analyzed as the sum of two relaxation processes, assuming a Debye process for the first and a Cole - Cole process for the second. It is an often observed fact that molecules with an as well longitudinal as perpendicular component of the dipole moment exhibit two seperate relaxation ranges also in the isotropic phase [15, 16].

Comparing the loss curves in the isotropic and nematic state (see Figs. 9, 10) one realizes the shift of f_{R1} to lower frequencies, as predicted by the theory [17], and the nearly constant f_{R2}. Further cooling lets disappear the low frequency relaxation from the available frequency window. At the transition N/S_C the

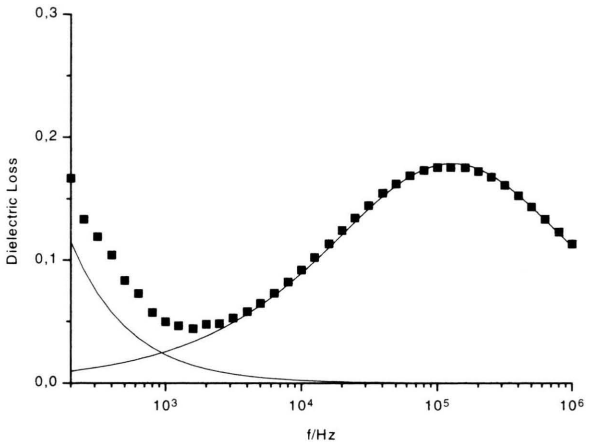


Fig. 7. Dielectric loss at 3 °C for **P7**; fit parameters: $\Delta_2 = 0.67$, $h = 0.62$, $f_R = 1.28 \cdot 10^5$ Hz, $A = 2.26 \cdot 10^1$ Hz.

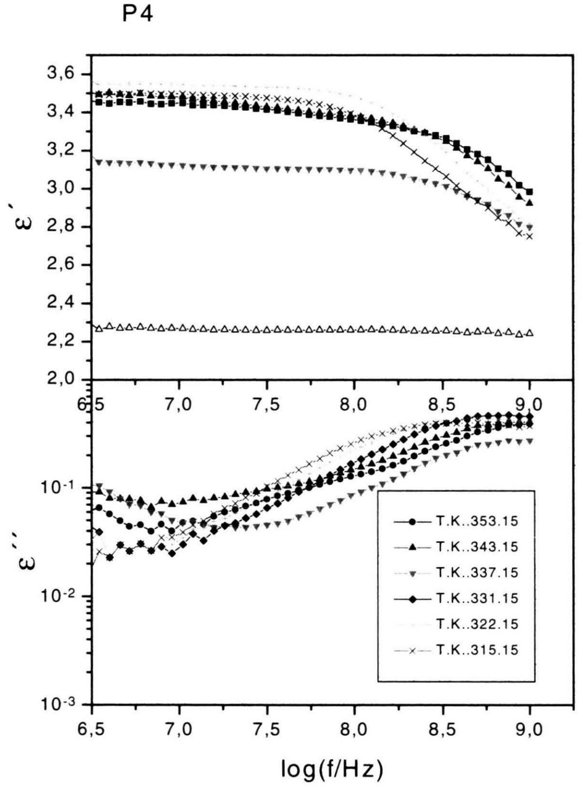


Fig. 8. Experimental curves of **P4** in the high frequency range (1 MHz - 1 GHz, HP 4191).

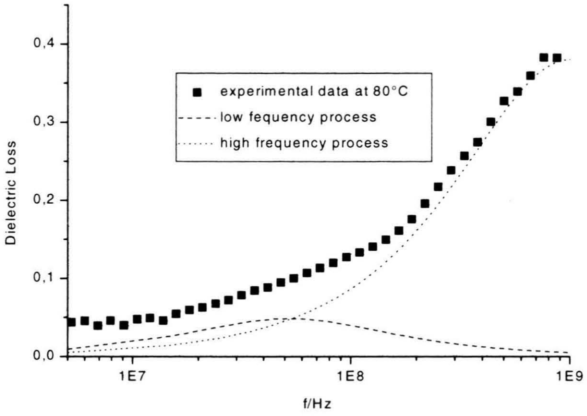


Fig. 9. Experimental data of **P4** at 80 °C (Is) fitted to two relaxation processes: $\Delta_1 = 0.097$, $f_{R1} = 5.19 \cdot 10^7$ Hz, $h_1 = 1$, $\Delta_2 = 0.81$, $f_{R2} = 1 \cdot 10^9$ Hz, $h_2 = 0.96$.

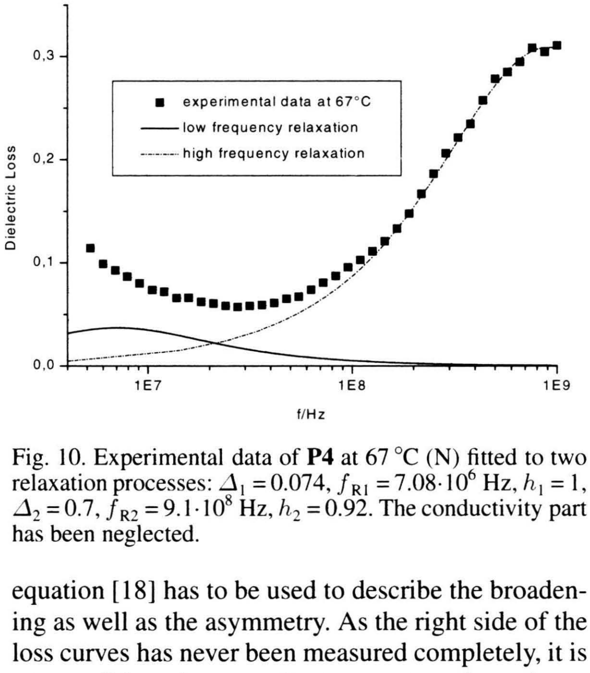
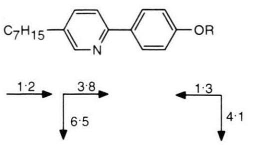


Fig. 10. Experimental data of **P4** at 67 °C (N) fitted to two relaxation processes: $\Delta_1 = 0.074$, $f_{R1} = 7.08 \cdot 10^6$ Hz, $h_1 = 1$, $\Delta_2 = 0.7$, $f_{R2} = 9.1 \cdot 10^8$ Hz, $h_2 = 0.92$. The conductivity part has been neglected.

increment Δ_2 increases from 0.7 to 1.0 while the Cole - Cole parameter h_2 stays constant at 0.9. Passing the transition into the S_F phase, the measured curves start to become asymmetrical and the Havriliak - Negami equation [18] has to be used to describe the broadening as well as the asymmetry. As the right side of the loss curves has never been measured completely, it is not possible to interpret the temperature dependence of the asymmetry parameter. That is why this parameter was kept constant at 0.9. There is no doubt that the high frequency process $\underline{2}$ in the isotropic and liquid crystalline phases is caused by the reorientation of perpendicular components of the dipole moment. But it is necessary to clear up whether the relaxation in the crystalline state is caused by the same molecular motion. That is why a simple dipole vector analysis [13] has been done and the quotient of increments Δ_2 in the isotropic and crystalline state has been related to

Table 3. Relation of dielectric increments Δ_2 and perpendicular components of the dipole moment μ_2.

	$\Delta_2 = \varepsilon_{02} - \varepsilon_{03}$	$\mu_2/10^{-30}$Cm	$\frac{\Delta_{\text{is}}}{\Delta_{\text{Cr}}}$	$\left(\frac{\mu_{2\text{ges}}}{\mu_{2\text{OR}}}\right)^2$
isotropic	0.75	$\mu_{2\text{ges}} = 7.7$	3.75	3.5
crystalline	0.2	$\mu_{2\text{OR}} = 4.1$		



$$\mu_1 = 1.2 + 3.8 - 1.3 = 3.7 \cdot 10^{-30}\ \text{Cm},$$
$$\mu_2 = \sqrt{4.1^2 + 6.5^2} = 7.7 \cdot 10^{-30}\ \text{Cm},$$
$$\mu_{2\text{OR}} = 4.1 \cdot 10^{-30}\ \text{Cm}.$$

the whole perpendicular component μ_2 and the perpendicular component of the alkoxy group $\mu_{2\text{OR}}$ as illustrated in Table 3.

Since in the isotropic state the molecules and in the crystalline state the crystallites are statistically distributed, one expects the same increments on the condition that the same molecular reorientation takes place. We noticed a significantly larger increment in the isotropic phase, which hints to a relaxation of a single part of the molecule in the crystalline phase. From the rough agreement of the quotient of increments and the quotient of dipole moments we conclude that the relaxation in the crystalline state is caused by rotations of the alkoxy group. From the slope of the Arrhenius - plots the activation energies E_A of process $\underline{1}$ in the S_C phase and the activation energies of process $\underline{2}$ in the crystalline state have been calculated, as listed in Table 4. In the other liquid crystalline phases the E_A values could not be calculated exactly because only few values of f_R have been available.

Table 4. Activation energies for both relaxation processes calculated from the slope of the Arrhenius plots.

	P4	P5	P6	P7	P8
process $\underline{1}$ S_C E_A / kJmol^{-1}	140±2	130±2	125±2	117±2	
process $\underline{2}$ Cr E_A / kJmol^{-1}	75±5		100±5	150±5	70±5

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