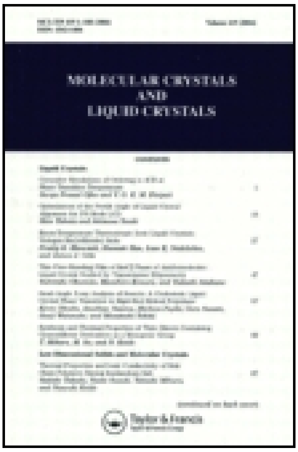

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Broadband Dielectric Spectroscopy on Ferroelectric Liquid Crystalline Polymers

A. Schönfeld [a] , F. Kremer [a] , H. Poths [b] & R. Zentel [b]
[a] Max Planck Institut für Polymerforschung Ackermannweg 10, 55128, Mainz, FRG
[b] Institut für Organische Chemie, Universität Mainz Becherweg 18 - 20, 55128, Mainz, FRG

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BROADBAND DIELECTRIC SPECTROSCOPY ON FERROELECTRIC LIQUID CRYSTALLINE POLYMERS

A. SCHÖNFELD*, F. KREMER*, H. POTHS**, R. ZENTEL**
* Max Planck Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz, FRG
** Institut für Organische Chemie, Universität Mainz
Becherweg 18 - 20, 55128 Mainz, FRG

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Abstract: The collective and molecular dynamics of ferroelectric liquid crystalline side group polasiloxanes has been investigated be use of broadband dielectric spectroscopy (10^{-2}Hz - 10^{9}Hz). In the lower frequency range ($<10^{6}$Hz) two collective relaxations, Goldstone - and soft - mode, could be observed. They are assigned to the fluctuations of the phase and the amplitude of the helical superstructue, respectively. In the high frequency regime (10^{6}Hz - 10^{9}Hz) *one* dielectric relaxation, the β - relaxation, is found. It is assigned to the hindered rotation (libration) of the mesogene around its long molecular axis. It shows an Arrhenius - like temperature dependence with no deviations at the phase transition S_A/S_C^* . A dilution of the mesogenes causes a decrease of the collectivity but remains the local dynamics uninfluenced.

INTRODUCTION

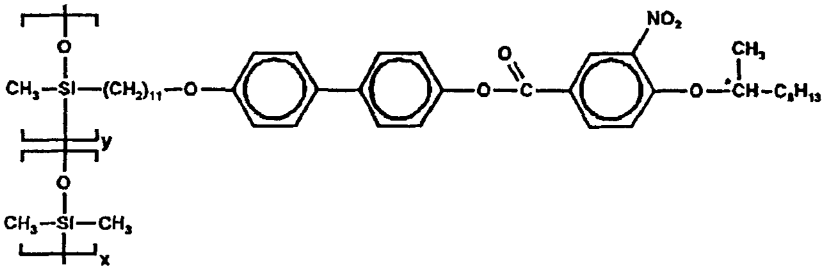
Since liquid crystalline compounds were found to have ferroelectric properties in chiral tilted smectic phases (for example S_C^* - phase)[1], there have been many affords to understand and optimize their ferroelectric behaviour (high saturation polarization, short switching times etc.). Besides a lot of synthetical work [2] and structure investigations [2] the molecular and collective dynamics of low molecular weight ferroelectric liquid crystals (FLC) has been investigated by several techniques as NMR [3], light scattering [4], dielectric spectroscopy [5-7] and is well understood. In 1984 the first ferroelectric liquid crystalline polymers were synthesized [8]. These materials combine the properties of low molecular weight FLC with the typical properties of polymers. Further on the liquid crystalline phases were stabilized by the polymer main chain which leads to much broader mesophases than in the analogous low molecular weight compounds. The combination of both the ferroelectric and the polymeric properties leads to new applications, for example as flexible displays [9]. For such applications the dynamical behaviour has also to be understood. But investigations of the local and collective dynamics of polymeric FLCs are still sparse.

In this paper we present broadband dielectric spectroscopy investigations (10^{-2}

to 10^9Hz) on ferroelectric liquid crystalline side group polysiloxanes. In order to check the influence of the polymer main chain on the dynamical behaviour of the mesogenes we extended our investigations beside the homopolymer (each repeating unit contains a mesogenic side group) to 'diluted' copolymers with different amount of mesogenes (not each repeating unit contains a mesogenic side group). Diluting polymeric side group polysiloxanes improves the possibilities of aligning the samples. The saturation polarization of these samples varies nearly linear with the mol - fraction of the mesogenes. As by X-ray measurements [10] a linear increase of the layer thickness is found in the smectic phases these substances are treated by a phase separation model, which means that the polymer main chain is located between the smectic layers. Increasing the amount of siloxane main chain ('diluting') leads only to an increse of the polysiloxane layer between the smectic layers and should result in a linear dependence of the measured layer thickness from the degree of dilution as it is found experimentally.

EXPERIMENTAL

To cover the frequency regime from 10^{-2} to 10^9Hz three different measurement systems were combined [11], (i) a frequency response analyser Solartron Schlumberger FRA1260 which was supplemented with a high impedance preamplifier of variable gain (10^{-2} to 10^6Hz), (ii) a Hewlett Packard Impedance analyser HP4192A (10^2 to 10^7Hz) and (iii) a Hewlett Packard coaxial reflectometer HP4191A (10^6 to 10^9Hz). The applied AC - measurement field was 1V for all measurements. In order to orient the polymers in the bookshelf geometry [12], custom made, rubbed, polyimide - coated metal electrodes (diameter 5mm, spacing 20μm) were employed. These capacitors enabled us to measure from DC up to 1GHz in *one* capacitor arrangement. The synthesis of the polymers is described elsewere [10]. The phase sequence was determined with DSC (Perkin Elmer DSC-2C,DSC), X-Ray measurements (Siemens TT 500 Goniometer) and polarizing microscopy. The molecular weights were determined by analytical GPC against polystyrene standards.
The following samples were investigated:



sample	x	y	M_W	M_N	P_S $[\frac{nC}{cm^2}]$	phase sequence
1	3.2	1	23000	14000	104	g 0 S_X 46 S_C^* 98 S_A 144 is.
2	1.1	1	53000	27000	130	g 13 S_X 54 S_C^* 124 S_A 168 is.
3	0.5	1	51000	29000	161	g 20 S_X 72 S_C^* 138 S_A 182 is.
4	0	1	28000	13000	211	g 21 S_X 57 S_C^* 161 S_A 183 is.

For the quantitative analysis the data were fitted with a generalized relaxation function according to Havriliak and Negami [13]

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + (i\omega\tau)^\alpha)^\gamma} \tag{1}$$

where τ is the mean relaxation time and ω the angular frequency of the outer electric field. ϵ_∞ and ϵ_S are the real parts of the dielectric function with $\omega\tau \gg 1$ and $\omega\tau \ll 1$, respectively. α and γ are constants describing the symmetric and asymmetric broadening, respectively. At frequencies below 10^4Hz an additional conductivity contribution was observed. It was fitted with the power law

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0}\omega^{s-1} \tag{2}$$

where σ_0 and s are fitting parameters and ϵ_0 is the permittivity of free space.

RESULTS AND DISCUSSION

In the frequency regime from 10^{-2} to 10^9Hz three dielectric loss processes can be observed (fig.1). Two of them (Goldstone - and soft - mode) occur at frequencies below 1MHz. Their huge dielectric losses indicate their collective character. In the frequency regime above 1MHz one dielectric relaxation is found. Its comparable low dielectric loss underlines the local character of this relaxation process, which is not restricted to the liquid crystalline phase. In the following we will first focus on sample 1 and than compare the four different poymers

Collective dynamics of FLC - polymers

In the frequency range below 1MHz the dielectric spectrum is dominated by one very huge relaxation (Goldstone - mode), which is restricted to the S_C^* phase (fig.2). It is assigned to the fluctuation of the phase of the helical superstructure. Comparing this process with the Goldstone - mode in the analogous low molar mass compound the relaxation is shifted nearly two decades to lower frequencies. Additionally the Goldstone - mode shows a pronounced temperature dependence while in low molar mass FLCs this process usually is only weakly temperature dependent. Superimposing a DC - bias field unwindes the helical superstructure. By this the Goldstone - mode can be suppressed continuously (fig.3). In the unwound state a second loss process (soft - mode) becomes observable again. In order to study the soft - mode behaviour in more detail the measurements were repeated with a

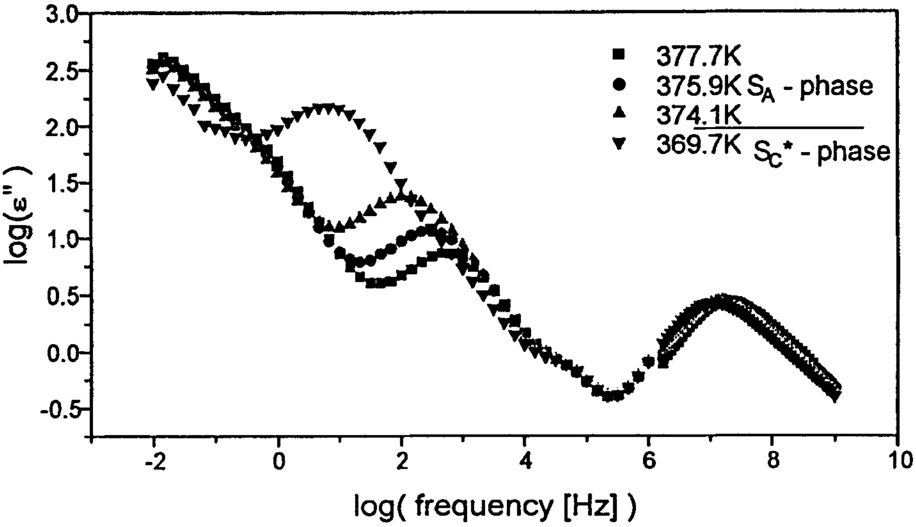


Fig. 1: log(ϵ'') *vs.* *log(frequency) measured over 11 decades for sample 1. The experimental error is estimated to be not larger than the size of symbols, the slope between* 10^4 *Hz and* 10^5 *Hz is due to an artefact of the measurement system.*

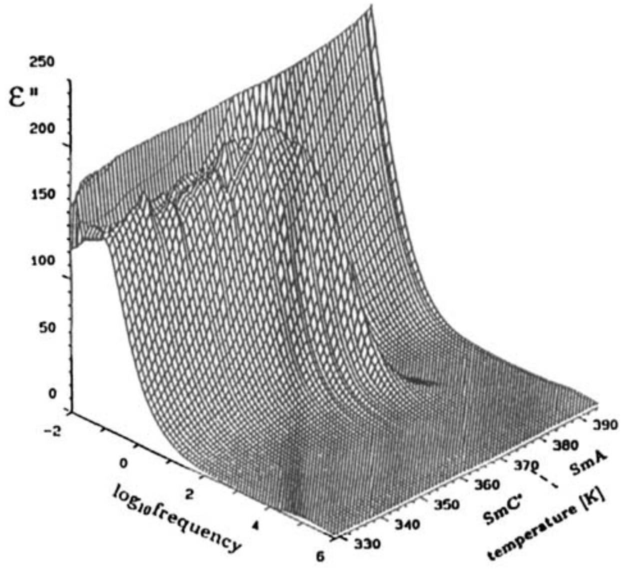


Fig. 2: *The Goldstone - mode in a polymeric FLC (sample 1).*

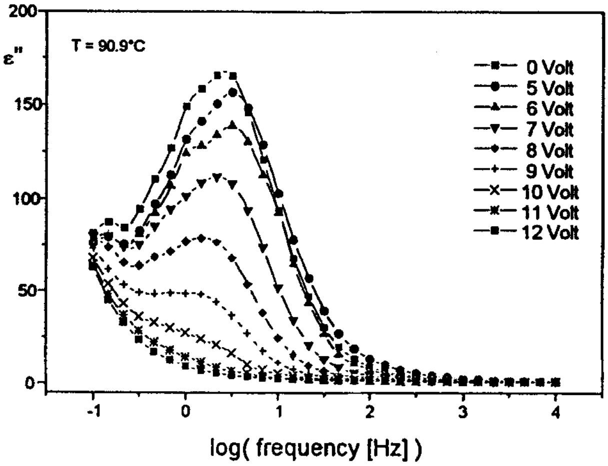


Fig. 3: *Superimposing a DC - bias field the Goldstone - mode can be suppressed continuously (sample 1), sample thickness:* $10 \mu m$.

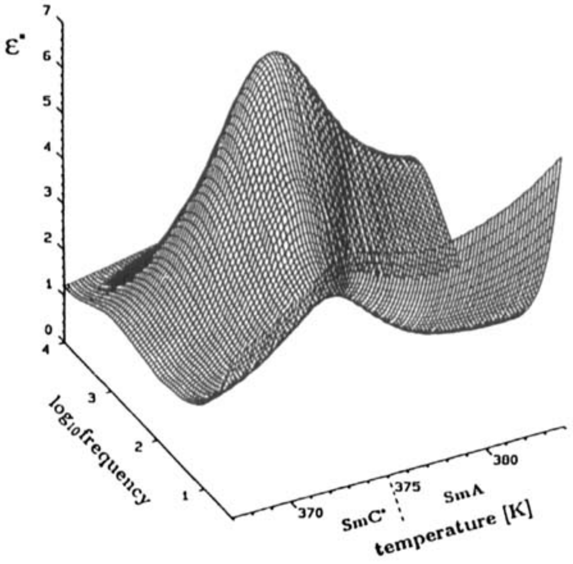


Fig. 4: *The soft - mode in a polymeric FLC (sample 1),* $E = 15 \frac{kV}{cm}$, *sample thickness:* $10 \mu m$.

superimposed DC - bias field (fig.4). The soft - mode, which is assigned to the fluctuation of the tilt, increases in the S_A - phase, has a maximum at the phase transition S_A/S_C^* and decreases in the S_C^* - phase. As the phase transition S_A/S_C^* is of second order the following theoretical predictions for the soft - mode dynamics near this transition have to be fullfilled: (i) The frequency position of the maximum dielectric loss should obey a Curie Weiss law, (ii) for this temperature dependence the slope in the S_C^* - phase should be twice as much as in the S_A - phase, (iii) for the inverse of the dielectric strength a similar Curie - Weiss temperature dependence is predicted.

In low molar mass FLCs these predictions are well fulfilled [7]. In order to check how comparable this dyanamical behaviour is in the polymeric compounds, the experimental data were fitted by use of the generalized relaxation function according to Havriliak and Negami (1). The inverse of the dielectric strength shows a comparable temperature dependence (fig. 5a) as predicted and as it is found for low molar mass FLCs. The frequency of the maximum ϵ'' only correspondes in the S_A - phase. Although the soft - mode should increase in its frequency position in the S_C^* - phase, it remains at nearly the same frequency position. This may be due to viscosity effects from the polymer main chain or from an insufficient supression of the Goldstone - mode. Additionally the phase transition occurs not as sharp as for low molar mass compounds, but this is a general feature of polymeric FLCs.

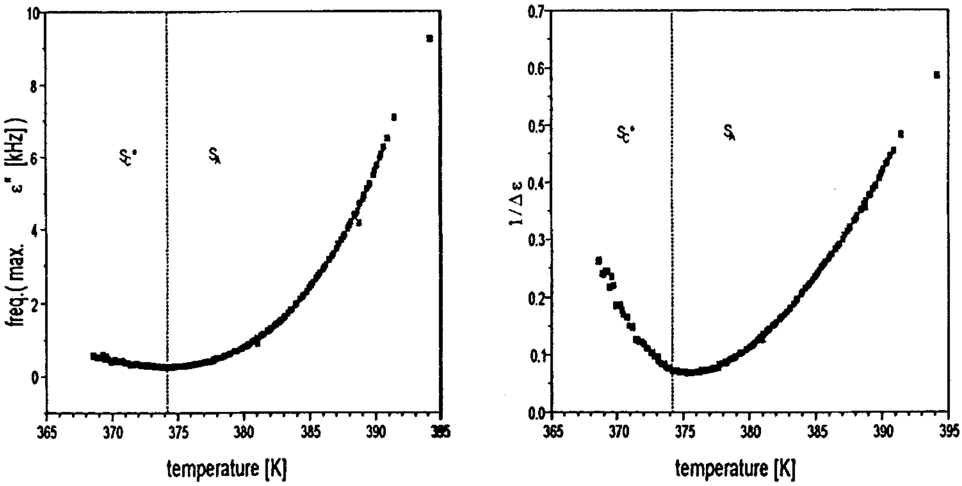


Fig. 5: *a.) Frequency of the max.* ϵ'' *vs. temperature b.) inverse dielectric strength vs. temperature (sample 1),* $E = 15\frac{kV}{cm^2}$*, sample thickness:* $10\mu m$.

Molecular dynamics of FLC - polymers

In the frequency regime above 1MHz *one* dielectric loss process - the β - relaxation

- can be observed (fig. 6). It is assigned to the hindered rotation (libration) of

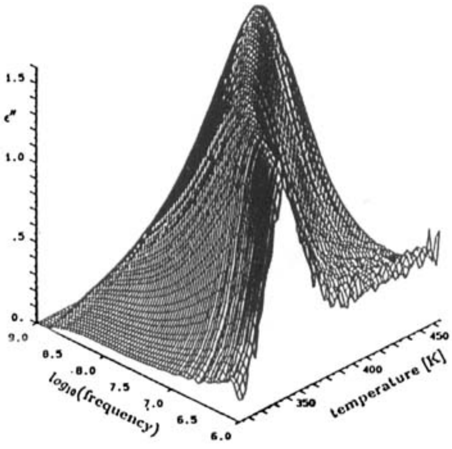


Fig. 6: *The β - relaxation in a polymeric FLC (sample 1), sample thickness: 20μm.*

the mesogene around its long molecular axis and has a comparable low intensity as expected for a local process. The measured loss curves can be well described with the Havriliak - Negami equation (1). The temperature dependence of the mean relaxation time τ and the dielectric strength $\Delta\epsilon$ is shown in fig. 7. The relaxation time shows no discontinuities at the phase transition S_A/S_C^* , especially there is no slowing down observable. By cooling down from the isotropic phase and by entering the S_C^* - phase, the dielectric strength $\Delta\epsilon$ increases, because due to the formation of the bookshelf geometry the aspect angle of the dipole moment interacting with the outer electric field changes. By the same argument there is a small step at the phase transition S_A/S_C^* . As the alignment in the high frequency measurements is only partially achieved, these steps are not as pronounced as for low molar mass systems.

Influence of diluting the polymers

Taking diluted copolymers, i. e. not each repeating unit contains a mesogenic side group, the samples are easier to align, because of the more flexible main chain. Even for the highest degree of dilution (only 25% mesogenes) a comparable phase sequence occurs. The saturation polarization shows a nearly linear dependence on the mol - fraction of mesogenes (fig. 8).

In order to investigate how this influences the collective dynamics of the samples, we measured the soft - mode behaviour of the four different polymers. The temperature dependence of their frequency positions is shown in fig. 9. All the samples show

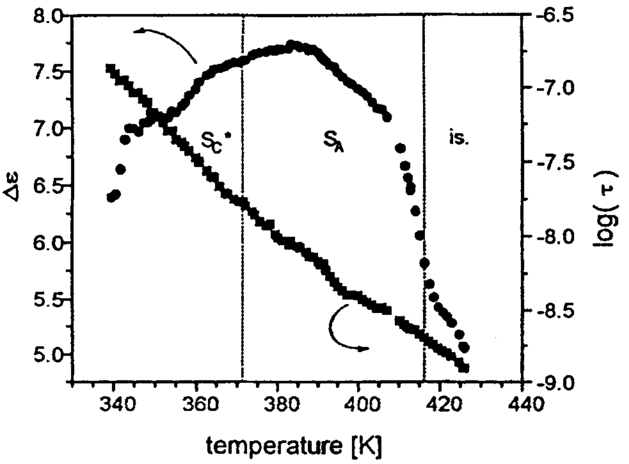


Fig. 7: *Temperature dependence of the dielectric strength (•) and the logarithm of the relaxation time (□) for the β - relaxationof sample 1.*

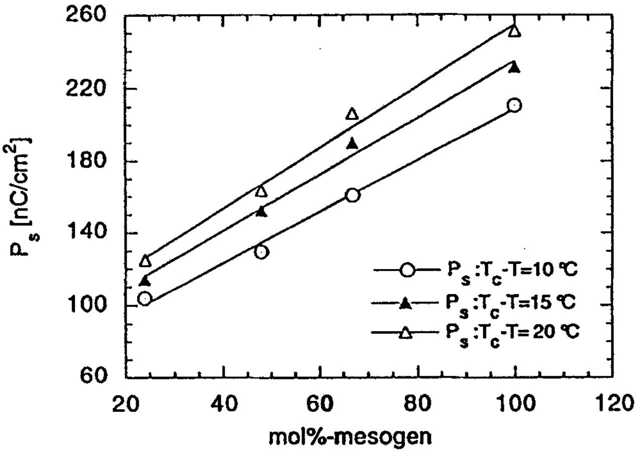


Fig. 8: *Dependence of the spontaneous polarization on the mol - fraction of mesogenes.*

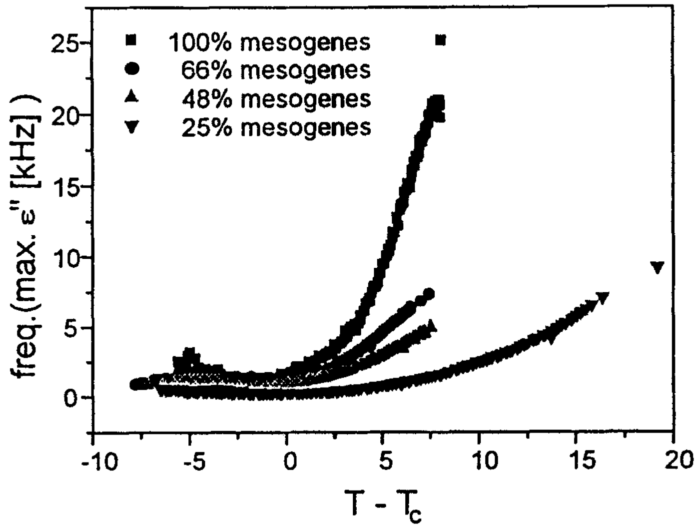


Fig. 9: *Critical slowing down for the diluted polymers.*

the expected critical slowing down. Comparing the degree of dilution, the critical slowing down shows a systematic change. The more diluted the the systems are the less pronounced the critical slowing down occurs. As the shift of the process to lower frequencies is due to an increase of the collectivity of the tilt fluctuations, the dilution decreases the collectivity. A less pronounced collectivity, however, influences both, the dynamic - (critical slowing down) and the static properties (spontaneous polarization). Comparing the absolute values of the relaxation times, it seems suprising that the concentrated homopolymer shows a faster fluctuation than the more mobile diluted systems. But one has to take into account that the absolute temperatures of the phase transition S_A/S_C^* differs up to $63K$. As the tilt fluctuation is a thermally activated process one can not compare the absolute relaxation times of two samples which differ in the absolute temperature by $63K$. It is possible that such a higher thermal activation overcompensates the less mobility in the more concentrated polymers. It is worth mentioning that the dielectrically oserved soft - mode relaxation confirms well with the response times obtained from measurements of the electroclinic effect (fig. 10).

In the high frequency regime (10^6Hz - 10^9Hz), where the local dynamics takes place, no influence of the dilution can be observed as expected (fig. 11). All the samples show the hindered rotation around the long molecular axis (β - relaxation). As this is a very local process it is not influenced by collectivity.

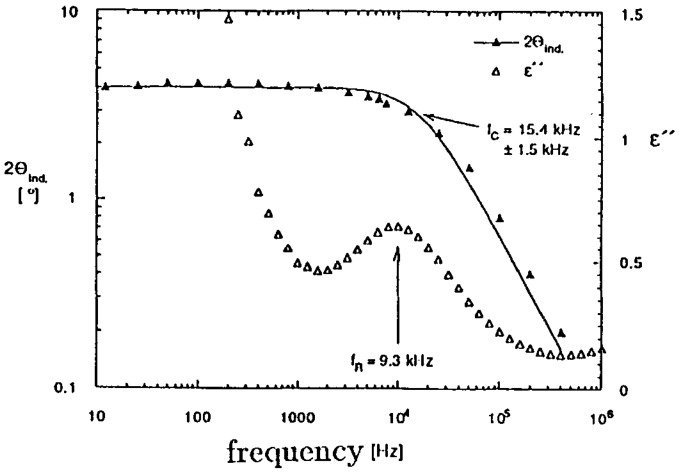


Fig. 10: *Comparison of the dielectricallay observed soft - mode with frequency dependent measurements of the electroclinic effect (sample 1).*

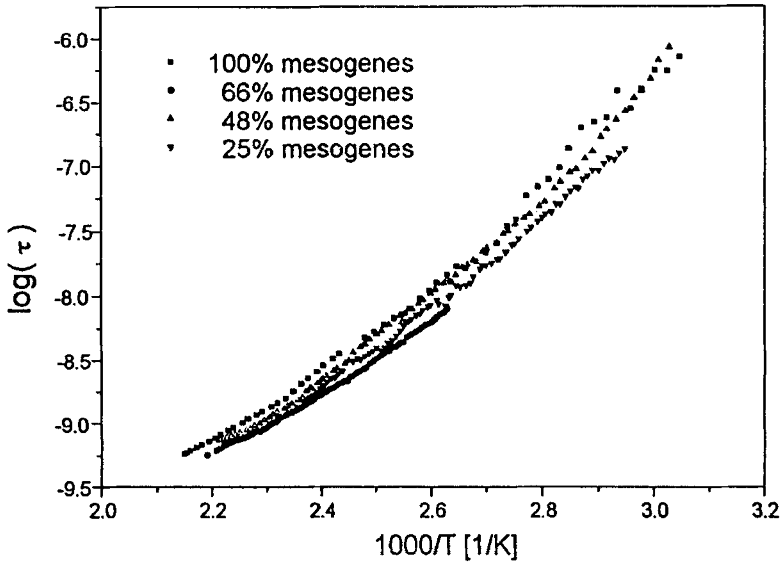


Fig. 11: *Activating plot for the high frequency relaxation of the diluted polymers.*

CONCLUSION

By use of broadband dielectric spectroscopy (10^{-2}Hz to 10^9Hz) the collective and molecular dynamics of ferroelectric liquid crystalline polymers can be analysed. Below IMHz two collective relaxations (Goldstone - an soft - mode) can be observed. The Goldstone - mode is assigned to the fluctuations of the phase of the helical superstructure. It can only be observed in the ferroelectric S_C^* - phase. The soft - mode is assigned to the fluctuation of the amplitude of the helical superstructure. Near the phase transition S_A/S_C^* the soft - mode shows a critical slowing down.
In the high frequency range (10^6Hz to 19^9Hz) *one* relaxation process, the β - relaxation, can be observed. It is assigned to the hindered rotation (libration) of the mesogene around its long molecular axis. The β - relaxation shows an Arrhenius - type temperature dependence. At the phase transition S_A/S_C^* no deviations could be observed.
A dilution of the polysiloxanes, i. e. not each repeating unit contains a mesogenic side group, leads to a less pronounced critical slowing down of the soft - mode. This can be understood in terms of lower collectivity of the tilt fluctuation caused by the dilution. The high frequency relaxation remains uninfluenced by the dilution as expected for a very local relaxation process.
Although their are slight differences the dynamics of ferroelectric liquid crystalline side group polysiloxanes is fully comparable to that of the analoguous low molar mass compounds.

REFERENCES

1. R. B. Meyer, L. Liebert, L. Strzlecki, P. J. Keller; J. Phys. (Paris) Lett. **36**, L69 (1975)
2. C. B. Mc Ardle, 'Side Chain Liquid Crystal Polymers' ,Blackie Publishing Group, Glasgow 1989
3. A. Yoshizawa, H. Kikuzaki, T. Hirai, M. Yamane; Jpn. J. Appl. Phys. **28**, 1988 (1989)
4. J. Muševic, R. Blinc, B. Žeks, C. Filipič, M. Čopič, A. Seppen, P. Wyder, A. M. Levanyuk; Phas. Rev. Lett. **60**,1530 (1988)
5. F. Gouda, G. Andersson, S. T. Lagerwall, K. Skarp, B. Stebler, T. Carlsson, B. Žekš, C. Filipič, A. Levstik; Liq. Crys. **6** (1989) 219
6. A. M. Biradar, S. Wrobel, W. Haase; Phys. Rev. A **39**, 2693 (1989)
7. A. Schönfeld, F. Kremer, R. Zentel; Liq. Cryst. **13**, 403 (1993); F. Kremer, A. Schönfeld, A. Hofmann, R. Zentel, H. Poths; Polym. Adv. Techn. **3**, 249 (1992)

8. V. P. Shibaev, M. Z. Kozlovsky, L. A. Beresnev, L. M. Blinov, N. A. Plate; Polymer Bull. **12**, 299 (1984)

9. K. Yuasa, S. Uchida, T. Sekiya, K. Hashimoto, K. Kawasaki; Polym. Adv. Techn. **3**, 205 (1992)

10. H. Poths, R. Zentel; Liq. Cryst., in press

11. F. Kremer, D. Boese, G. Meier, E. W. Fischer; Prog. Coll. & Pol. Sci. **80**, 129 (1989)

12. N. A. Clark, S. T. Lagerwall; Appl. Phys. Lett. **36**, 899 (1980)

13. S. Havriliak, S. Negami; J. Polym. Sci. **C14**, 89 (1966)