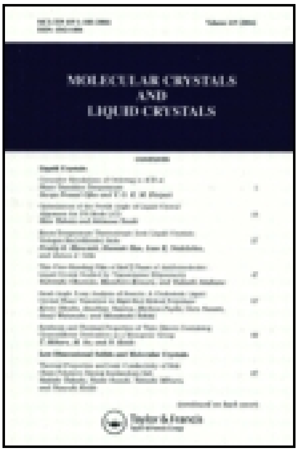

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DIELECTRIC PROPERTIES OF COMPOUNDS EXHIBITING C_α^* PHASE AND THEORETICAL ANALYSIS OF THE RESULTS

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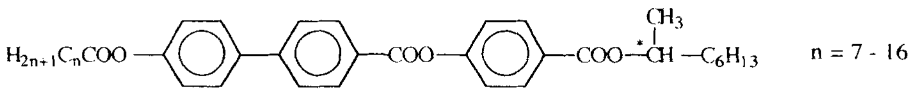
Abstract Dielectric measurements of a homologous series MHPnCBC exhibiting different phase sequences have been carried out. The results and the comparison with the theoretical predictions of the phenomenological model are presented for the dielectric behaviour in the smectic C_α^* phase.

INTRODUCTION

Since the existence of three subphases, smectic C_α^* , smectic C_γ^* and AF phase was discovered in addition to the antiferroelectric smectic C_A^* phase in MHPOBC[1], MHPOCBC[2], MHPBC[3], their structures have been studied extensively[3]. In order to gain a deeper insight into the structure of these phases, and their dependence on the length of the molecules, a homologous series MHPnCBC based on the structure of MHPOCBC with varying the alkyl chain length of the non chiral part from n=7 to n=16 has been synthetized. The exhibited phase sequence as well as the dielectric behaviour were analyzed and comparison with the theoretical predictions is drawn.

COMPOUNDS

A homologous series of liquid crystalline compounds based on the structure given in Fig.1 has been synthetized according to standard methods. The structural variations are restricted to a variation of the alkyl chain length on the non-chiral end of the molecules. The variation has been realized for n=7-18, where n gives the number of carbons in the alkyl chain. Transition temperatures were determined via differential scanning calorimetry, while phases have been identified with methods of polarization



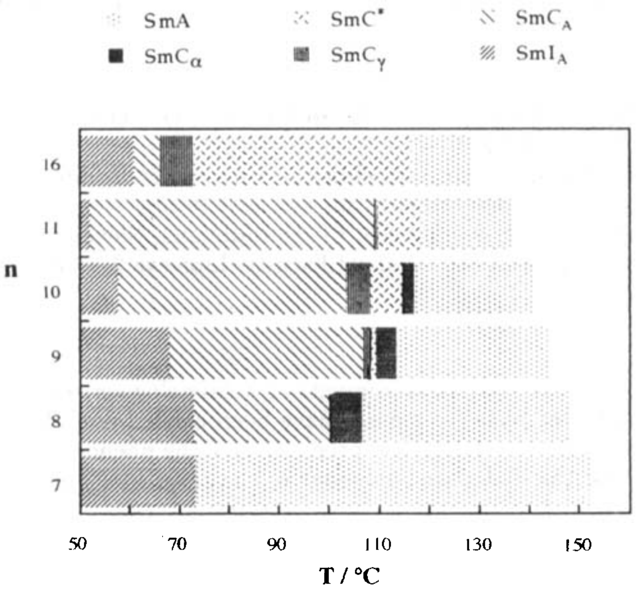


Figure 1: Phase sequences of the homologous series MHPnCBC.

microscopy. Details of synthesis and of physico-chemical properties will be reported elsewhere.

In Fig.1 the phase sequences and the transition temperatures for some compounds of the series are given. One of the homologous (n=8: MHP8CBC = MHPOCBC) has been synthetized for the first time by Isozaki et al.[2].

Three compounds of the homologous series exhibit smectic C_α^* phase (n=8,9,10). The width of the smectic C_α^* phase narrows with increasing chain length. The compounds with n=9, 10, 11 and 16 exhibit the smectic C_γ^* phase, which appears only in connection with the smectic C^* phase. Increasing the alkyl chain length (> 10) as well as decreasing (< 8) reduces the number of phases. The increase stabilizes the smectic C^* phase, while the Sm A phase is stabilized by shortening the alkyl chain length.

EXPERIMENTAL RESULTS

The frequency and temperature dependence of the complex dielectric constant were measured with an HP-4194A impedance analyser in the frequency range between 100Hz and 15MHz. The amplitude of the measuring voltage was set to 0.1V in every case. For the measurements under a biasing field a d.c. voltage up to 40V was applied. The investigations presented here have all been performed in commercially available cells (E.H.C.) with a cell gap of 10μm and a unidirectionally rubbed polyimide coating for planar alignment. To achieve homogeneous alignment we took advance of the EHD-effect by applying a triangular wave of $5V/\mu m$, 20Hz, and performing several heating cycles over the smectic C_α^* to Sm A transition. Temperature control was done by a Mettler FP82 hot stage. The dielectric measurements have been performed in cooling direction only.

In order to obtain the relaxation frequency f_{relax}, the dielectric spectra were fitted according to the Havriliak-Negami equation[4].

Since the variation of the alkyl chain length changes the phase sequence, it was possible to study the smectic C_α^* phase with phase transitions to smectic C_A^* , C^* and - as will be pointed out later - AF. In this contribution we restrict ourselves to results obtained on two compounds, namely MHP8CBC and MHP9CBC.

In Fig. 2a the 3D dielectric spectra of MHP8CBC are given as ϵ'' (dielectric loss) versus logarithm of frequency (measured in Hz) of the applied field and temperature. Two maxima in ϵ'' are clearly seen. One is appearing at the transition from smectic A to smectic C_α^* phase and the other one just above the smectic C_α^* to C_A^* transition. The temperature independent absorption at the high frequency end of the spectra is due to the cell relaxation. In Fig.2b the temperature dependence of the lg(f_{relax}) and the respective dielectric strength ($\Delta\epsilon$) are shown. The low temperature maximum is strongly influenced by an applied d.c. field in contrast to the high temperature maximum: the low temperature maximum decreases and shifts to higher temperatures with increasing d.c. field strength, while the high temperature one remains at the same temperature. At fields of 2V/μm the low temperature maximum changes into a shoulder and dissapear. In Fig.3 the dielectric loss versus lg(f) measured under different biasing fields for two temperatures is given. The higher temperature corresponds to the Sm A to smectic C_α^* transition, Fig.3a, and the lower temperature is chosen where the maximum dielectric loss in the low

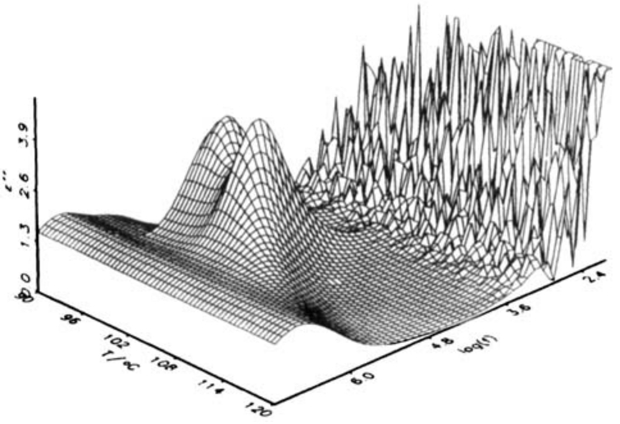


Figure 2a: Dielectric spectra of MHP8CBC: dielectric loss (ϵ'') versus temperature and the logarithm of frequency of the applied field.

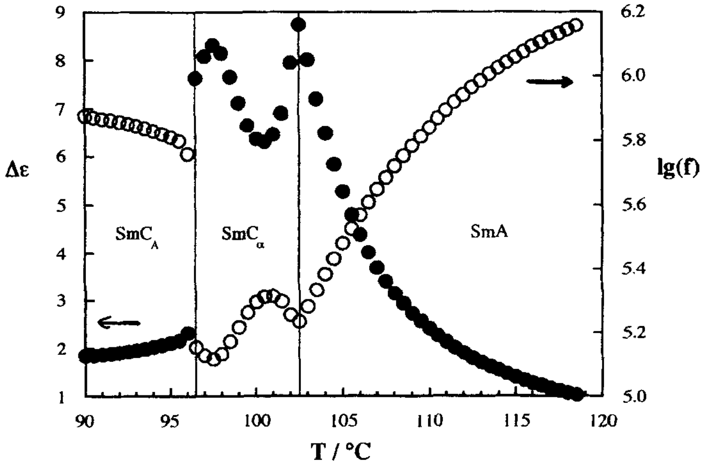


Figure 2b: Dielectric strength ($\Delta\epsilon$) and lg(f_{relax}) versus temperature of MHP8CBC.

temperature region of the smectic C_α^* phase occurs without field, Fig.3b.

In the Sm A phase lg(f_{relax}) and $\Delta\epsilon$ exhibit the usual temperature dependent behaviour. The absorption of the smectic C_A^* phase can be either due to the reorientation of the molecules (ferroelecric phason mode^6), or less probably due to the changes of the magnitude of the tilt (ferroelectric amplitudon mode^6). The third possibility to explain this absorption is the molecular reorientation around the short

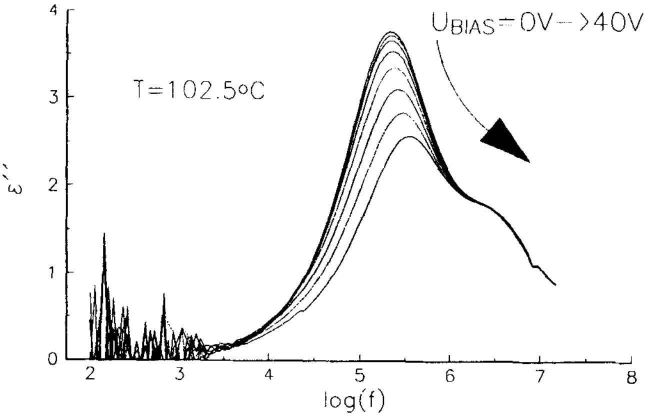


Figure 3a: The effect of the d.c. field on the dielectric loss in the smectic C_α^* phase at 102.5°C.

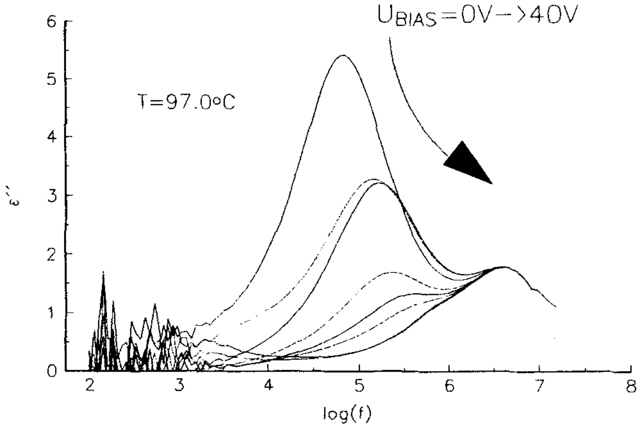


Figure 3b: The effect of the d.c. field on the dielectric loss in the smectic C_α^* phase at 97.0°C.

axes of the molecules.

Fig. 4a shows the dielectric spectra of MHP9CBC. In the spectra five different regions can clearly be distinguished. The respective phase transitions correspond to the DSC measurements. Additionally to the observed phases in MHP8CBC two phases occur between smectic C_α^* and the C_A^* phase. The lower one could be identified as the smectic C_γ^* phase by optical methods. In this phase two typical modes[5]

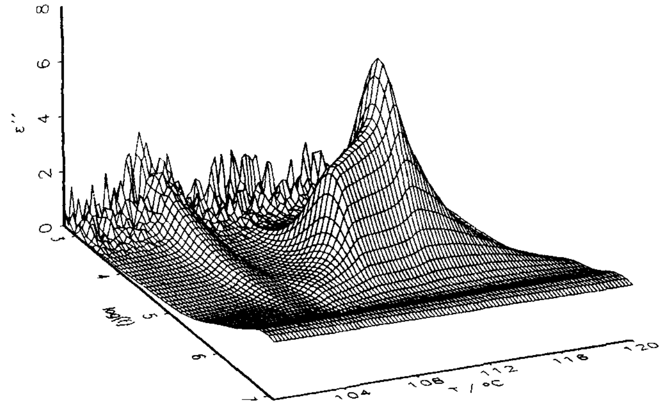


Figure 4a: Dielectric spectra of MHP9CBC: dielectric loss (ϵ'') versus temperature and the logarithm of frequency of the applied field .

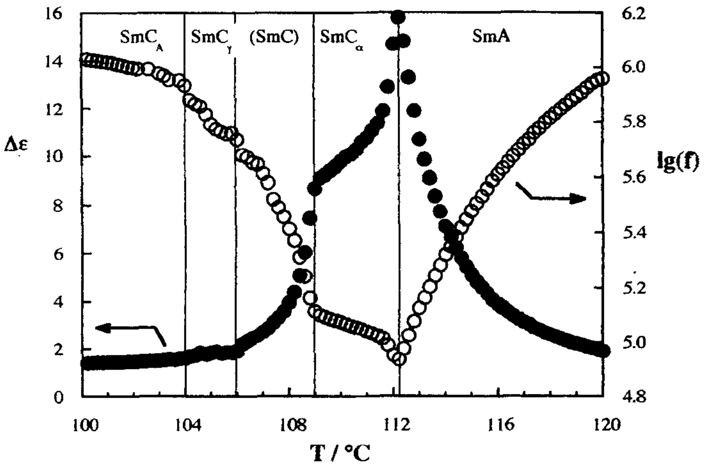


Figure 4b: Dielectric strength ($\Delta\epsilon$) and $\lg(f_{relax})$ versus temperature of MHP9CBC.

(low and high frequency) have been observed. The high frequency absorption is due to the out of phase phason mode[6] and the low frequency absorption, which can partly be seen on Fig. 4a and 5a, is due to the Goldstone mode in smectic C^*_γ phase[5,6]. On Fig. 4b and 5b only the high frequency mode can be seen because of the frequency range presented on these two figures. The comparison of the dielectric spectra of MHP9CBC and MHPBC[7] (see Fig.4a and Fig.5a) indicates that the phase between

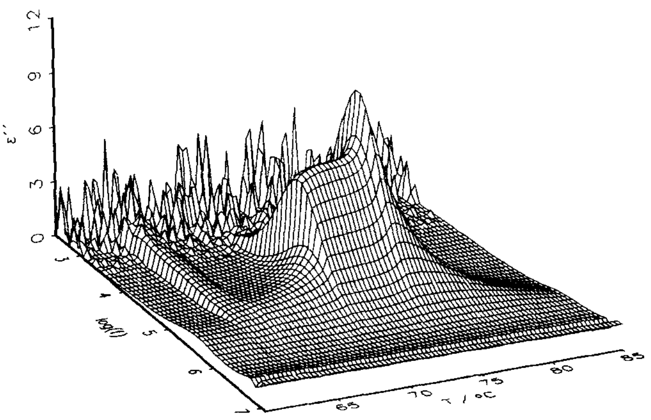


Figure 5a: Dielectric spectra of MHPBC: dielectric loss (ϵ'') versus temperature and the logarithm of frequency of the applied field.

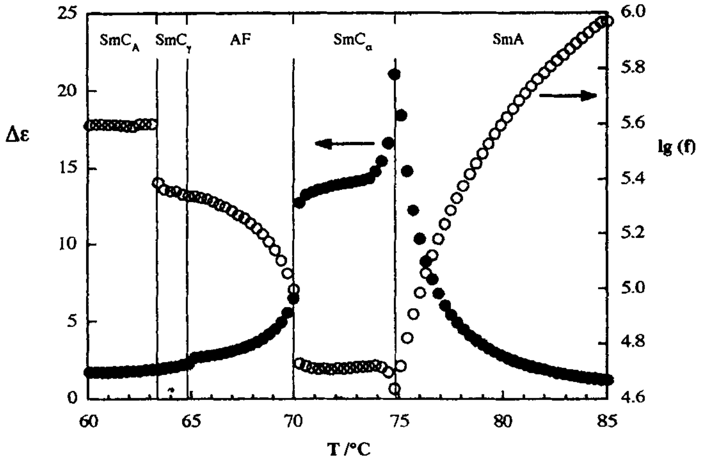


Figure 5b: Dielectric strength ($\Delta\epsilon$) and lg(f_{relax}) versus temperature of MHPBC.

smectic C_α^* and smectic C_γ^* is of the same type as the AF phase found in MHPBC. These compounds (MHP9CBC and MHPBC) show only one maximum in ϵ'' observable at the transition from the smectic C_α^* to the Sm A phase. At the transition from smectic C_α^* to the presumed AF phase the dielectric spectra of both compounds exhibits only a shoulder in ϵ''.

THEORETICAL ANALYSIS

Dielectric properties of the smectic C^*_α phase can be at least qualitatively understood by employing the discrete phenomenological model with competing interactions[8]. In the model, the free energy of the system is expressed in terms of the tilt order parameters defined for each layer. It is assumed that intralayer interactions leading to the phase transition from isotropic to the tilted phase are much stronger than interlayer interactions, which are of achiral and chiral character. When the achiral interactions between next nearest layers favour antiparallel orientation of order parameters in the next nearest layers and the nearest layers interactions are weaker, frustration appears. These competing interactions between nearest and next nearest layers give rise to the helicoidally modulated smectic C^*_α phase with a short pitch[8]. The structure is similar to the structure of smectic C^* phase, which is modulated due to the chiral interactions, except that the pitch is much shorter.

A dielectric response of the short pitch helicoidal structure is therefore similar to the response of the C^* phase[9], only the magnitude of the response is much smaller, because the critical wave-vector for the smectic A - C^*_α transition is much larger than for the smectic A - C^* transition. The dielectric response in the smectic C^*_α phase should therefore consist of the two contributions: the Goldstone mode part and the soft mode part. The soft mode part is expected to contribute to the dielectric response only close to the smectic A - smectic C^*_α transition, while at lower temperatures in the smectic C^*_α phase the response should consist only of the Goldstone mode part.

Such a prediction is in agreement with observed data, which show maximum in the dielectric response at the smectic A - smectic C^*_α transition. This maximum cannot be suppressed by external electric field, because it consists of the soft mode part and the electric field cannot affect fluctuations in the magnitude of the tilt very much. At lower temperatures the measured dielectric response is of the Goldstone mode type and can be therefore suppressed by electric field.

Such a simple model cannot explain the observed maximum in the Goldstone mode response within the smectic C^*_α phase above the smectic C^*_A - C^*_α transition, as it is also not able to explain different observed phase sequences. Higher order terms would lead to the temperature dependent effective interactions between nearest layers and next nearest layers and therefore allow for different phase sequences and different temperature dependeces of the dielectric response. When the interactions between nearest layers favour antiferroelectric ordering and the interactions between next nearest layers change from competing to noncompeting ones with growing tilt, the sequence of phases Sm A $\leftrightarrow C_{\alpha}^{*} \leftrightarrow C_{A}^{*}$ as observed in MHP8CBC (Fig.1), is possible.

Also, when the nearest layer interactions with lowering temperature become weak and next nearest interactions favour antiparallel orientation, the structure with pitch extending over four layers only, occurs. This structure has strong antiferroelectric character and could correspond to the observed AF phase in MHP9CBC (Fig.4 and 5). Because the structure develops by winding of the C_{α}^{*} phase, it exists in temperature region below the smectic C_{α}^{*} phase and the dielectric response has to decrease from smectic C_{A}^{*} phase to AF continuously, as presented on Fig.4 and 5. Dielectric response of the AF phase is expected to be larger than in the smectic C_{A}^{*} phase, which is purely antiferroelectric (Fig.2, 4 and 5). To the high temperature peak of dielectric response in the homologue MHP9CBC (Fig.4) contribute the Goldstone and the soft mode as in the homologue MHP8CBC (Fig.2).

CONCLUSIONS

The results obtained from DSC and dielectric measurements of the homologue series MHPnCBC have been analyzed according to the phenomenological theory. The behaviour of the dielectric response with and without d.c. electric field can be explained referring to the structures of the respective phases. The structures as well as the phase sequences could be obtained by taking into account temperature dependence of the interactions between nearest and next nearest layers.

REFERENCES

1. A.D.L.Chandani, Y.Ouchi, H.Takezoe, A.Fukuda, K.Terashima, K.Furukawa, A.Kishi, Jpn.J.Appl.Phys, 28, L1261, (1989).
2. T.Isozaki, Y.Suzuki, I.Kawamura, K. Mori, N. Yamamoto, Y. Yamada, H.Orihara, Y.Ishibashi, Jpn.J.Appl.Phys, 30, L1573, (1991).
3. T.Isozaki, K.Ishikawa, H.Takezoe, A.Fukuda, Ferroelectrics, 147, 159 (1993) and references therein.
4. S.Havriliak, S.Negami, Polymer 8, 161 (1967).
5. M.Čepič, G.Heppke, J.-M.Hollidt, D.Lötzsch, B.Žekš, Ferroelectrics, 147, 121

(1993).

6. M.Čepič and B.Žekš, 3rd ECLC, Flims, Switzerland, (1993).
7. N.Okabe, Y.Suzuki, I.Kawamura, T.Isozaki, H.Takezoe and A.Fukuda, Jpn.J.Appl.Phys., 31, L793 (1992).
8. M.Čepič and B.Žekš, Proceedings of 15th ILCC, Mol.Cryst.Liq.Cryst., to be published.
9. R.Blinc, B. Žekš, Phys.Rev.A, 18, 740 (1978).