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INVESTIGATION OF 4'-[(S)-2-PROPOXYPROPOXY] PHENYL 4-(4-DECYLOXY) BENZOATE (PPPhDB) BY COMPLEMENTARY METHODS

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Abstract Dielectric, electrooptic, DSC calorimetry studies and texture observations have been carried out for 4'-[(S)-2 propoxypropoxy] phenyl 4-(4-decyloxy) benzoate in a wide temperature range. Dielectric spectra were taken in the frequency range from 10Hz to 10GHz. Electrooptic studies were performed on oriented SmC* phase. Texture observations and DSC calorimetry confirm the existence of a monotropic highly ordered S_3 phase. On the basis of TDS measurements and electrooptic studies this phase seems to be a highly ordered non-ferroelectric phase. Low frequency dielectric spectrum of the SmC* phase is complex and consists at least of two contributions which is typical of ferroelectric liquid crystals with high spontaneous polarization.

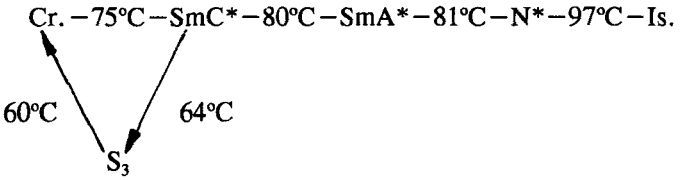
INTRODUCTION

Liquid crystals, including ferroelectric liquid crystals exhibit molecular dynamics, i.e. the reorientation around the short and long axis define their flow properties. The reorientation around the short molecular axis takes place in N, SmA, SmC, SmI, SmF and even in the highly ordered phases like SmB and SmJ[1]. As far as ferrolectric liquid crystals are concerned the reorientation around the long axis enables fast switching, especially in liquid like SmC*. It is important to know more about the molecular dynamics in SmC* phase as well as in other ferroelectric phases (SmG*, SmI*) and compare the results obtained by different methods.

In this paper we are dealing with a ferroelectric liquid crystal, 4'-[(S)-2 propoxypropoxy] phenyl 4-(4-decyloxy) benzoate (in short PPPhDB). On cooling this compound shows the following phase sequence: Is - N^* - SmA - SmC^* - S_3 - Cr. It seemed interesting to check whether the S_3 phase is also ferroelectric and liquid crystalline or not. Using complementary methods we hopefully solve this problem.

EXPERIMENTAL

Dielectric spectra were studied for PPPhDB showing the following phase diagram:



This substance was designed by the Boulder group[1].

The dielectric measurements were performed for both low and high frequencies regions. The perpendicular component of the complex electric permittivity was measured on planar aligned sample using HP 4192A impedance analyser in the frequency range from 10 Hz to 13 MHz[2]. The thickness of the sample was 10μm. The TDS spectrometer was used to measure dielectric spectra in the frequency range from 10 MHz to 10 GHz[3]. The dielectric spectra for perpendicular component were measured as a function of temperature covering all the phases. The alignment of the sample for high frequency dielectric measurements was obtained by means of a magnetic field of 0.6 T.

Tilt angle measurements were done using a home made equipment with WILMER PID controller, KZ 1405 function generator, calibrated heating stage and Karl-Zeiss Jena polarizing microscope (Jenapol). The aligment of the sample for electrooptic measurements and texture observations was done by means of A.C. fields using a Laboratory Compact Unit type PZL-1.

Electrooptic and low frequency dielectric measurements were performed on oriented thin layers using a commercial 10 μm-EHC cell.

Textures for various phases were observed on heating and cooling using Jenapol polarizing microscope. The photographs were taken using Praktica PLC 3 camera. The magnification of microscope was in this case 50.

The DSC measurements were made using High-Temperature Heat Flux Differential Calorimeter DSC 404 produced by NETZSCH. Several experimental series were carried out for various masses of the samples placed in aluminum crucibles. The heating and cooling rates were equal to 2K/min.

RESULTS AND DISCUSSION

DSC and polarizing microscopy measurements

These two methods were used to check transition temperatures and determine the types of the transitions. The DSC results obtained for PPPhDB on heating and cooling of the sample are shown in Figure 1. Figures 2 through 5 show the textures obtained for subsequent phases showing up on cooling the sample of PPPhDB. Figure 2 shows a typical cholesteric texture. As the temperature range of the SmA phase (Figure 3) is narrow it was difficult to obtain a uniformly aligned layer like in the case of FFP [4,5]. The oriented SmC* phase is switchable and the threshold voltage for unwinding the helix is comparatively low (ca. 1.5 V/10μm at 74.5°C). The texture of the S_3 phase (Fig.5) is stable under electric fields, which means that in this phase all molecular motions responsible for ferroelectric properties in the SmC* phase are frozen out. One should point out that there is a supercooling effect of the SmC*-S_3 transition as well as of the S_3- Cr.

Microscopic and DSC results are in good agreement. As is seen from Fig.1 the S_3 phase is shifted towards lower temperatures in comparison with literature data. In addition, the DSC data show that the SmC*- S_3 transition seems to be of the first order type.

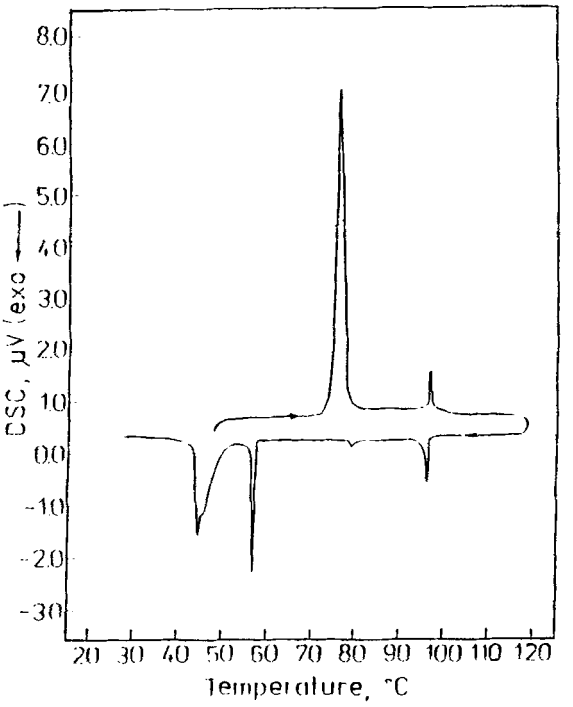


Fig.1. DSC results obtained for PPPhDB during heating and cooling processes.

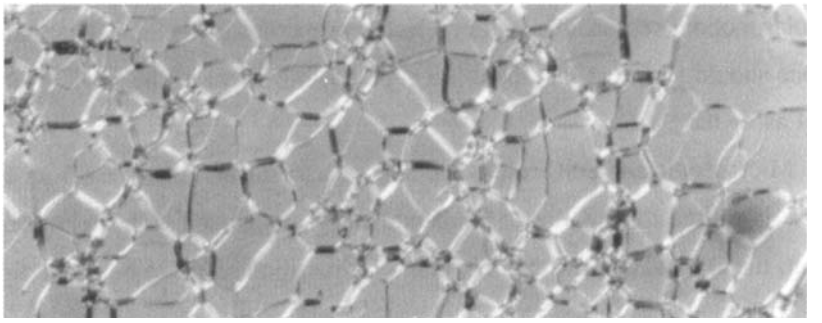


Fig.2 Texture of the cholesteric phase of PPPhDB. See Color Plate II.

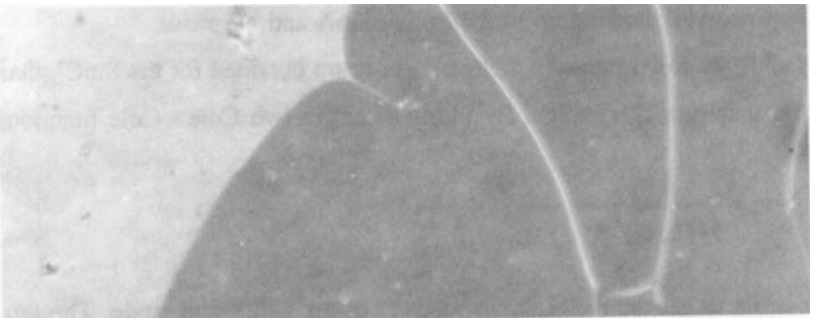


Fig.3. Orientational effects in the SmA phase
See Color Plate III.

Fig.4. Oriented SmC* phase (on the left side) and disordered SmC* (on the right side)
See Color Plate IV.

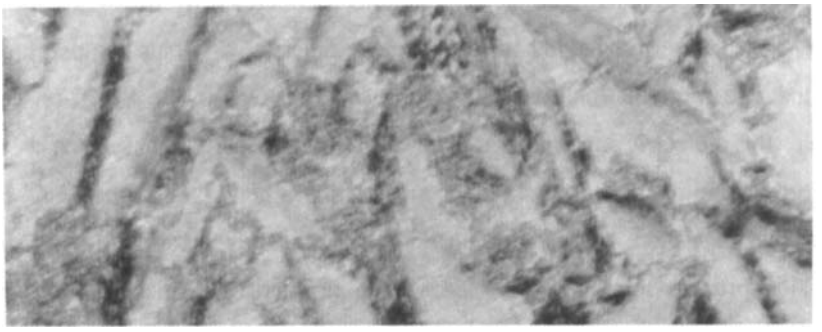


Fig.5. Texture of the S_3 solid modification of PPPhDB
See Color Plate V.

Dielectric relaxation spectroscopy

By using two experimental techniques it was possible to study the collective and molecular processes showing up in the SmC*, SmA and N* phase.

Fig.6 presents the low frequency dielectric spectrum obtained for the SmC* phase. As is seen this spectrum is complex. By fitting a sum of two Cole - Cole functions:

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1+(i\omega\tau_1)^{1-\alpha_1}} + \frac{\Delta\varepsilon_2}{1+(i\omega\tau_2)^{1-\alpha_2}} \quad (1)$$

it was possible to get the dielectric parameters of the Goldstone mode. The left hand side of the spectrum (Fig.6a) is disturbed by a strong conductivity absorption. This is due to a rather strong conductivity of the material studied ($\sigma \approx 5 \cdot 10^{-8}$ S).

One should explain that it was difficult to study the soft mode dielectric spectrum in the SmA and SmC* (below T_C).

Fig.7 shows how the Goldstone mode dielectric parameters behave at the SmA - SmC* and SmC* - S_3 transitions. As is seen there is no Goldstone mode in the S_3 phase.

The high frequency dielectric spectrum gives information about the reorientation of molecules around their long axis in all liquid crystalline phases. One of the important questions of molecular dynamics in liquid crystals is whether the reorientation around the long axis takes place in ferroelectric phases and/or it is restricted. Up to now this problem has not been solved uniquely[3,6,7,8].

Fig.8 presents Cole - Cole plots for the high frequency spectrum obtained for PPPhDB. Table I contains the dielectric parameters obtained by fitting a Cole -Cole function to the experimental data. If one plots $\Delta\varepsilon$ and ν_R versus temperature one notices that the reorientation around the long axis survives to the SmC* phase, and moreover, the dielectric increment appears to be bigger in this phase than at higher temperatures. The distribution parameter also seems to be bigger in the SmC* phase, which means that there might be a new high frequency relaxation process in this phase. This process may be connected with a non-uniform (biased) reorientation around the long axis.

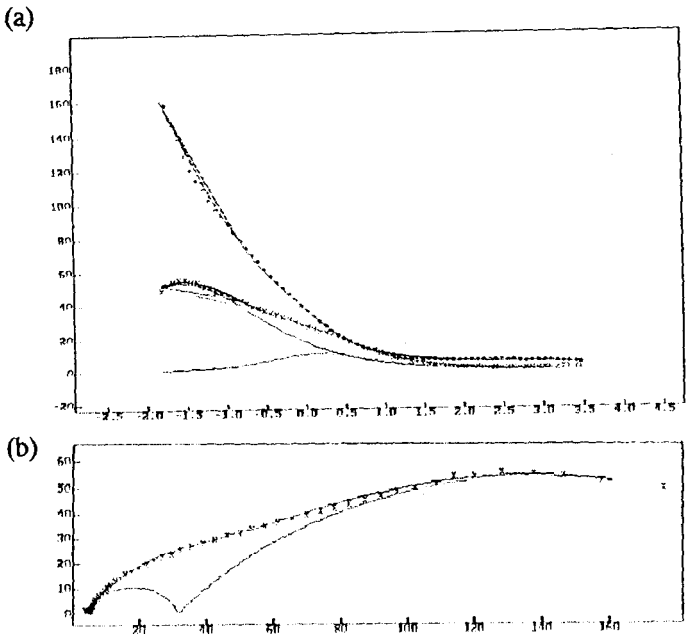


Fig.6 (a) Low frequency dielectric spectrum acquired for the SmC* phase of PPPhDB, (b) Cole-Cole diagram for the low frequency spectrum

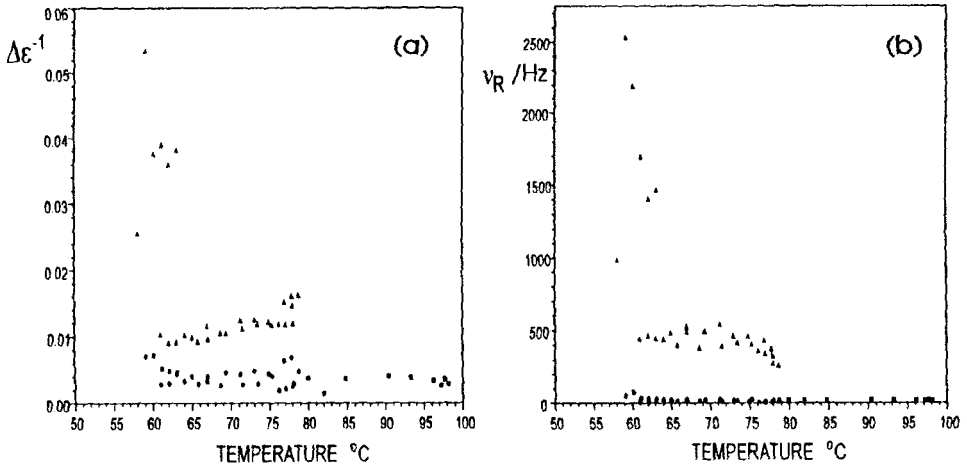


Fig.7. The Goldstone mode the inverse of dielectric increment (a) and crytical frequency (b) vs. temperature.

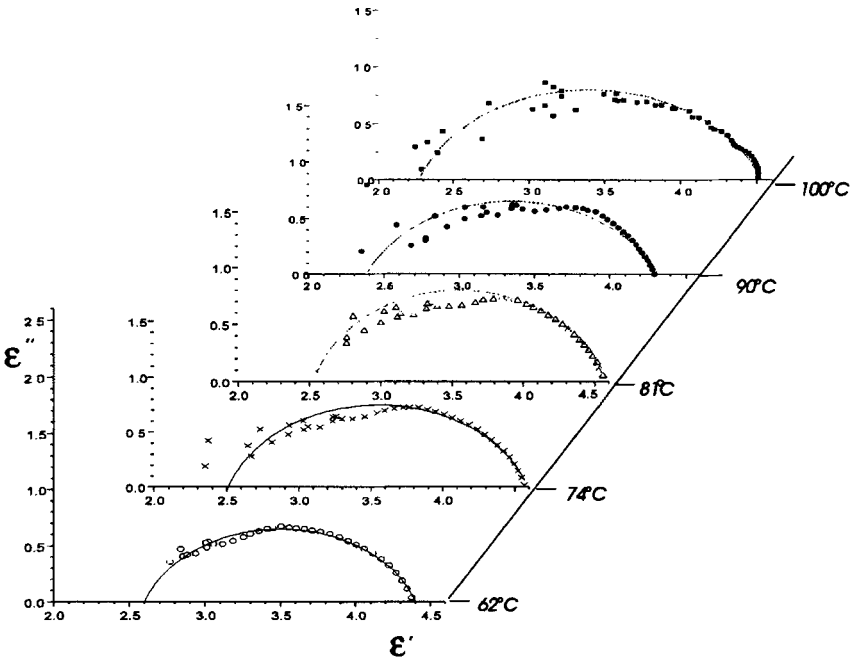


Fig.8. TDS dielectric spectra for all liquid crystalline phases

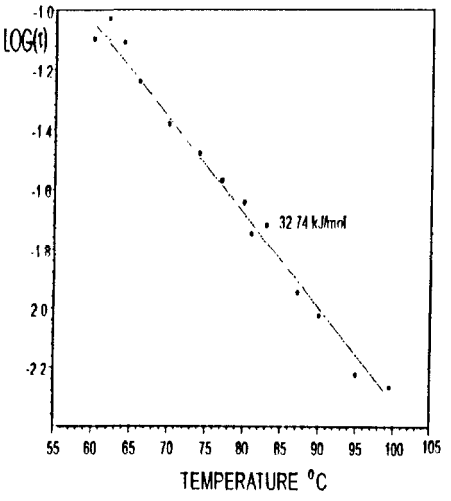


Fig.9. Temperature dependence of the relaxation time for the fast molecular process

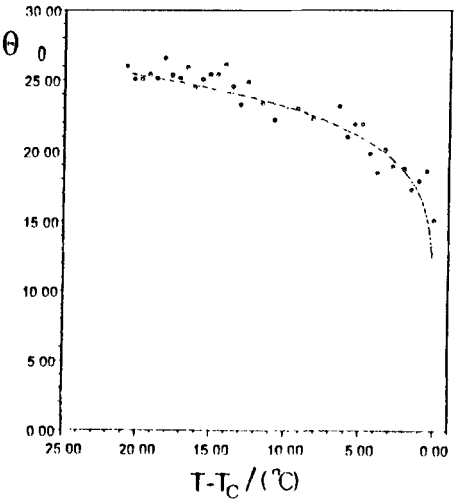


Fig.10. Tilt angle temperature dependence

Table I Dielectric parameters obtained by fitting Cole-Cole functions to the experimental data acquired in the high frequency range

Temp./°C	$\Delta\varepsilon$	τ/ns	α
100	1.92	0.12	0.16
95	1.94	0.11	0.15
90	1.74	0.13	0.17
87	1.79	0.12	0.15
83	1.84	0.18	0.19
81	2.01	0.17	0.17
80	2.13	0.19	0.19
77	2.17	0.21	0.21
74	2.18	0.23	0.22
70	2.24	0.25	0.23
66	2.17	0.29	0.25
64	2.12	0.33	0.26
62	2.10	0.36	0.26
60	1.58	0.33	0.26

If follows from the high frequency dielectric measurements (Fig.9) that the reorientation around the long axis is frozen out in the S_3 phase. The activation energy obtained from the Arrhenius plot for the SmA and SmC* phases is 32.74kJ/mol which is typical of reorientational motions around the long molecular axis in liquid crystalline phases. The S_3 - Cr transition is then between two solid modification.

Electrooptic measurements

In the SmC* it was easy to align the sample using a rectangular wave having amplitude of up to 30 $V_{p\text{-}p}$. At low frequences (down to 10^{-1}Hz) the switching between the two positions of the director ($+\vartheta_0$ and $-\vartheta_0$) was clearly seen and one could measure the tilt angle ϑ_0 . Fig.10 presents our results. The following function was fitted to the experimental points (see Fig.10):

$$\vartheta_0(T\text{-}T_C) = C + A(T\text{-}T_C)^{\beta} \qquad (2)$$

The fit yielded the following parameters values: A=16, C=0.468, β=0.136. One can only comment that the SmC*- SmA transition is not, in this case, continous as predicted by mean field theory.

One should add that there was no switching observable in the S_3 phase. At the SmC* - S_3 transition the aligned texture breaks up into small disordered areas (Fig.5) which do not move under A.C. fields.

CONCLUSIONS

1. DSC calorimetry, dielectric relaxation, texture observation and electrooptic studies show that the S_3 phase is a solid phase, in which over-all molecular motions are frozen out.

2. In the SmC* phase the high frequency dielectric spectrum is broader which may indicate a non-uniform (biased) reorientation of molecules around their long axes. The low frequency spectrum is complex and influenced by at least two molecular processes.

Acknowledgements

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