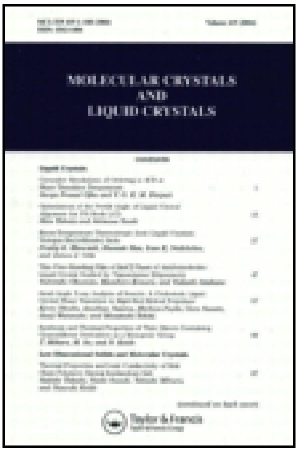

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ANOMALOUS DIELECTRIC BEHAVIOUR IN ORTHOPALLADATED FERROELECTRIC LIQUID CRYSTALS

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Abstract A ferroelectric ortho-palladated dimer derived from chiral imines with two chiral terminal chains in the aromatic ring has been characterized by dielectric permittivity, polarization, X ray and heat capacity measurements. An anomalous behaviour has been detected in the low temperature range of the SmC* phase. A new molecular arrangement has been found on cooling prior to the crystallization not detected before by DSC experiments.

INTRODUCTION

Among the high efforts made in order to synthesize compounds presenting ferroelectric properties, a new class of mesogenic compounds incorporating transition metals can be point up [1,2]. These new materials show a variety of mesophases with unusual electrical, optical and magnetic properties.

Belonging to this new class, ferroelectric ortho-palladated dimers derived from chiral imines have been synthesized and characterized [3]. In this study , the authors show that in all the cases an increase in the number of chiral chains leads to a non proportional increase of the spontaneous polarization values together a decrease of the temperature range of the SmC*. On cooling the SmC* texture remains down to the crystallization while on heating the existence of a second crystalline phase, called K_2, before the SmC* phase has been detected by DSC measurements

In order to study this anomalous behaviour in the SmC* phase we performed a complete study by means of X ray , ac and DSC calorimetry and dielectric measurements in one of the compounds belonging to this serie, called R-A2, with two chiral terminal chains in the aromatic ring involved in the orthopalladation.

EXPERIMENTAL

Powder X-Ray diffraction patterns were obtained in a Guinier diffractometer (Huber 644) operating with a Cu Kα1 beam issued from a germanium momochromator. The sample was held in rotating Lindemann glass capillaries (ϕ=0.5 mm) and heated with a variable temperature attachment. The diffraction patterns were registered with a scintillation counter.

The cell for the dielectric and polarization studies was made of two gold plated brass electrodes (ϕ=12 mm) separated by a 60 μm thick annular teflon ring. They were treated with PVA to achieve planar alignment. The sample holder was held in a cryostat, wich screens the system. The cell was filled in the SmA phase. Temperature, dielectric and spontaneous polarization measurements were fully computer controlled. Measurements have been performed on heating and on cooling at a rate of 0.5 °C/min. The dielectric permitivity has been measured with the HP4192A impedance analyzer. The spontaneous polarization has been obtained using the triangular wave method.

Specific heat were performed using a high-resolution ac calorimeter. The details of the calorimeter has been described elsewhere [4]. In this case we use as sample holder a DSC can with 3.6 mg of sample. The selected frequency was 22 mHz around which linearity between the inverse ac signal and frequency was observed. Measurements were performed on cooling at 1.8 K/h and on heating at 1 K/h.

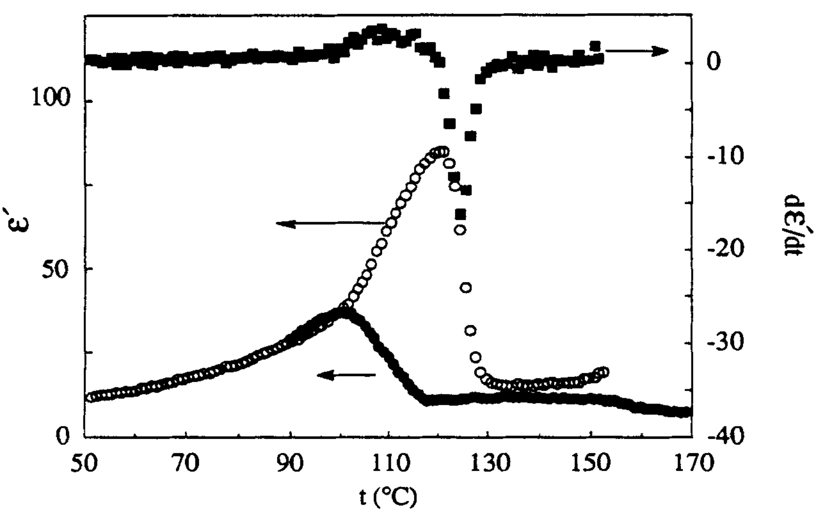

FIGURE 1 Dielectric permittivity

RESULTS AND DISCUSSION

Dielectric measurements show an anomalous behaviour in the low temperature region of the SmC* phase. In figure 1 we plot the dielectric permittivity on heating (open circles) and on cooling (close circles) at the same frequency (100 Hz). In the heating curve, there is a continuous and slow increase of the permittivity from 50 °C up to a maximum and then a sharp decrease down to 127 °C indicating the beginning of the SmC* phase. The DSC data show a peak at 103 °C associated with the transition between two crystalline phases called K_1 and K_2. Evidence of this phase transition can be obtained through the temperature derivative of the permittivity (close squares in figure 1) where a small hump around 103 °C can be seen, in agreement with the DSC run. On cooling, the temperature range of the SmC* phase is larger, reaching 117 °C, where a smooth increase starts , matching the heating curve at around 100 °C and following the same behaviour as the heating one. Then a large hysteresis behaviour in the crystal-SmC* transition has been detected. In both curves a small anomaly associated with the SmA-SmC* transition can be apreciated at around 157°C.

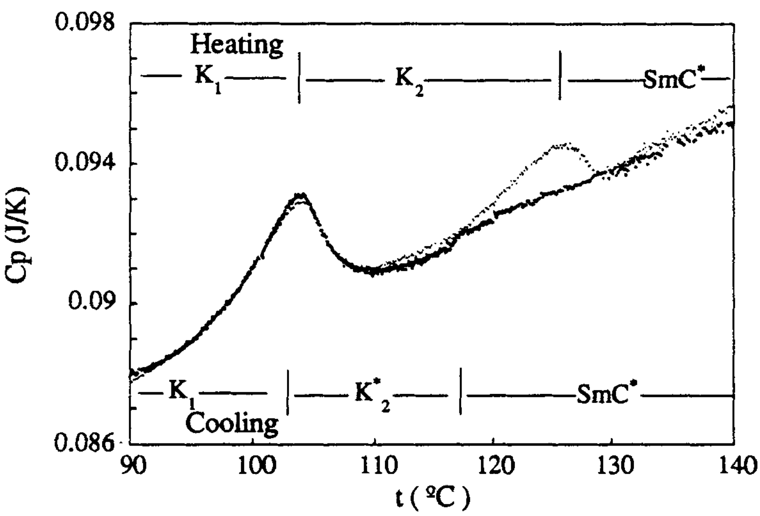

FIGURE 2 Heat capacity measurements.

This different dielectric behaviour on heating and on cooling has been analysed by ac calorimetry. In figure 2 both runs are shown in the interesting temperature region. In the cooling curve the SmC* phase seems to evolve down to about 117°C where a clear but

small decrease is present before the conversion to the K_1 phase. In this small temperature range (103°C-117°C) a new phase K_2* associated with the smooth increase of the permitivity can be see.This was not detected by DSC experiments.
A wider temperature range (103°C-127°C) in the heating run corresponds to the K_2 phase in accordance with dielectric measurements and DSC data . The small difference between the heat capacities of K_2 and K_2* and the shape of C_p during the conversion to the K_1 phase, seems to indicate that both phases can be almost the same.

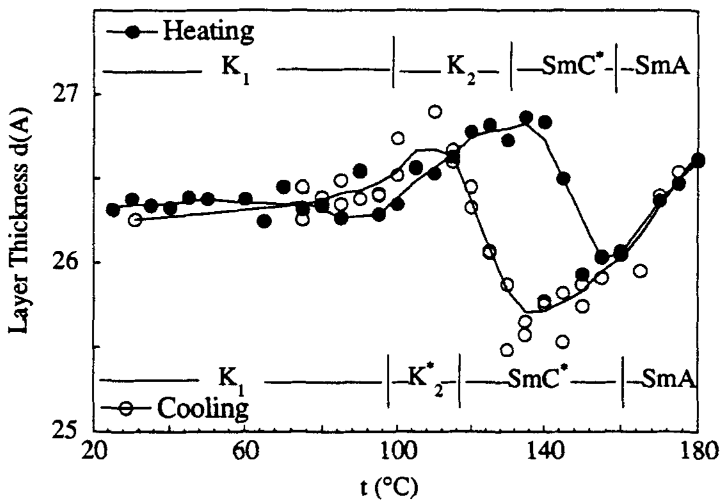

FIGURE 3 X-ray data

X-ray measurements are shown in figure.3. A jump in the layer thickness is observed around the temperature region where the K_2* phase exists and corresponds to a new molecular arrangement with a layer thickness similar to the K_2 one.

X-ray can give also information about the stability of the SmC* phase. Fast cooling from 160 °C (SmA phase) down to different temperatures and subsequent hold process produces an evolution of the layer thickness corresponding to the SmC* phase at these low temperatures to the thickness value of the crystal phase.The lower temperature, the larger time is needed to arrive to this increase of the thickness. For example after 14 h. at 50 °C the value corresponding to the extrapolation of the SmC* behaviour at this temperature remains stable.Nevertheless, in only half an hour at 125°C the layer thickness of the crystal phase has been obtained.

Spontaneous polarization is shown on cooling (open circles) and on heating (close circles) in figure.4. Spontaneous polarization appears on heating at 127 °C corresponding to the SmC* phase, but on cooling there is not any anomaly at 117 °C where the new phase K_2* starts, however the Ps value persists in this temperature range and also in the K_1 phase.

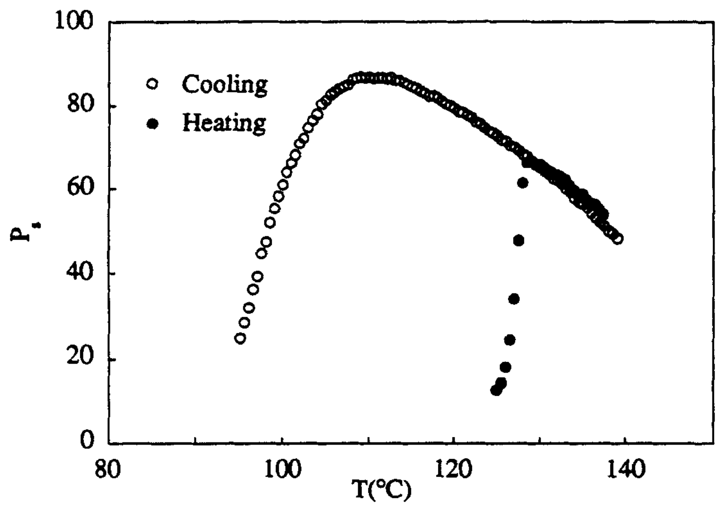

FIGURE 4 Spontaneous polarization

In conclusion , on cooling a new package (K_2*) prior to the crystallization has been confirmed, not detected by DSC measurements, with a layer periodicity similar to the K_2 phase detected in the heating run but with a non zero spontaneous polarization.

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