Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 583-591
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Phase Behaviour and Electrooptic Properties of a New Fluorinated MHPOBC Analogue

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A new MHPOBC analogue displaying ferroelectric and antiferroelectric properties has been studied by complementary methods. The dielectric measurements have been performed on a gold coated cell having thickness of 23 μm. In the antiferroelectric SmC_A^* phase two dielectric processes have been observed. Both these processes show Arrhenius type behaviour. Reversal current method has been applied to study temperature dependence of two polarization current peaks in the antiferroelectric phase. Temperature dependence of the spontaneous polarization in the ferroelectric and antiferroelectric phases has been studied and discussed in terms of the mean-field model.

Keywords: paraelectric; ferroelectric and antiferroelectric liquid crystalline phases; dielectric properties; spontaneous polarization

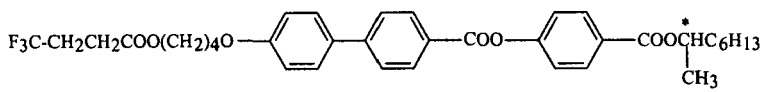
INTRODUCTION

During last decade a lot of experimental and theoretical works on antiferroelectric liquid crystals (AFLCs) have been done [1-5]. There are several papers about the dielectric modes behaviour in the transition region between ferroelectric and antiferroelectric phases [6-8]. The aim

of this paper is to study dielectric and electrooptic properties of a new MHPOBC analogue exhibiting ferroelectric and antiferroelctric phases in the phase diagram. DSC method has been used to study thermal behaviour of this substance. Dielectric and electrooptic methods allowed us to identify the liquid crystalline phases.

EXPERIMENTAL

The molecular structure and the phase transition temperatures of (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl 4'-[4-(4,4,4-trifluorobutanoyloxy) -but-1-oxy] biphenyl-4-carboxylate (in short MHP(3F)BBC) are presented in Fig. 1.



Cr. 88°C SmC_A^* 112°C SmC^* 116°C SmA^* 117°C Is.

Figure 1 Molecular structure and phase transition temperatures of the substance studied

Thermal behaviour of the compound was studied using Perkin-Elmer PYRIS 1 DSC apparatus. The instrument was calibrated by means of the melting points of indium and water. The samples were placed in aluminium crucibles. Empty aluminium crucible was used as a reference. The measurements were performed in the temperature range from 20 to 130°C with heating and cooling rates equal to 5°C/min.

The dielectric measurements were been performed by using computer controlled HP4192A impedance analyzer[9]. A gold-coated

cell having thickness of 23 μm was used for measurements of dielectric spectra.

Electrooptic measurements were performed on 7 μm-LINKAM cell by using Mettler – Toledo hot stage driven by FP900 controlling processor. Spontaneous polarization was measured versus temperature for different frequencies of driving triangular wave. The amplitude of voltage applied was up to V_{p-p}=150 V.

RESULTS AND DISCUSSION

DSC measurements

The DSC runs obtained in the present work for MHP(3F)BBC on heating and cooling of the sample are presented in Fig.2. As one can see on the DSC heating curve four anomalies are visible. They are also present on the cooling curve, in most cases shifted towards lower temperatures due to a hysteresis effect. The enthalpy changes connected with the observed

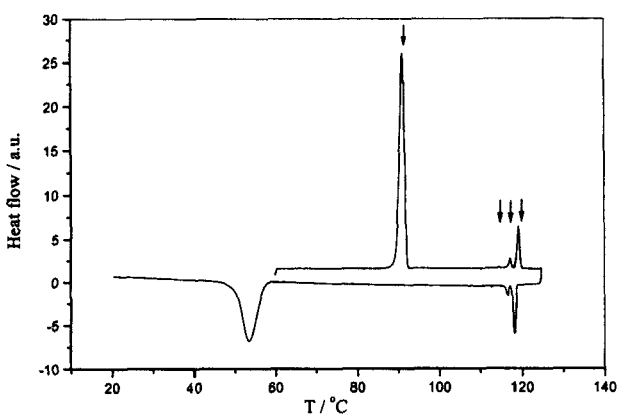


Figure 2 DSC runs for MHP(3F)BBC, heating and cooling rates equal 5 deg/min

phase transitions were calculated by numerical integration of the DSC anomalies. A linear background was previously subtracted. The transition temperatures of the substance studied are given with the accuracy of 0.1 °C and the enthalpy changes at the transitions are computed with the accuracy of about 5%.

Table I Transition temperatures and enthalpy changes obtained by DSC method for MHP(3F)BBC

	T (°C)	ΔH(kJ/mol)	Phase transitions
heating	91.0	40.90	Melting
	114.6	0.06	SmC_A^* - SmC^*
	117.3	0.85	SmC^* - SmA^*
	119.2	4.03	SmA^* - Is.
cooling	118.3		
	116.8		
	112.9		
	53.5		

From Table I it is seen that the melting enthalpy for the substance under investigation is significantly higher than those of the other phase transitions. The clearing point shows also higher enthalpy change than the transitions between the liquid crystalline phases. This can be explained by very small structural changes between the phases in the latter case. It is known that the transition enthalpies are directly connected with the structural changes at the phase transitions.

Electrooptic measurements

The reversal current method was used to measure spontaneous polarization versus temperature. Exemplary response current peaks vs. temperature for MHP(3F)BBC obtained at frequency 2 Hz are presented in Fig. 3. It is seen that in the antiferroelectric SmC_A^* phase two peaks

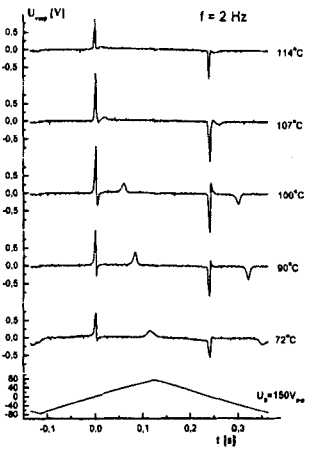


Figure 3 Exemplary response current peaks vs. temperature for MHP(3F)BBC

are observed. The higher peak - showing up at zero field - is connected with the field induced transition between ferroelectric and antiferroelectric states. The smaller one at a higher field is connected with further transition to another ferroelectric state [10]. The position of the smaller peak changes with temperature – it shifts towards lower fields with increasing temperature. Such peaks were found for other substances in several papers [1,10,11]. Spontaneous polarization versus temperature is presented in Fig.4. The values of spontaneous polarization for each peak were calculated by numerical integration. As is seen from Fig.4 the values of spontaneous polarization connected with the smaller and higher peak change with temperature and they are equal in the lower temperature range of the antiferroelectric SmC_A^* phase. According to the extended mean field model of the second order transition between ferro-

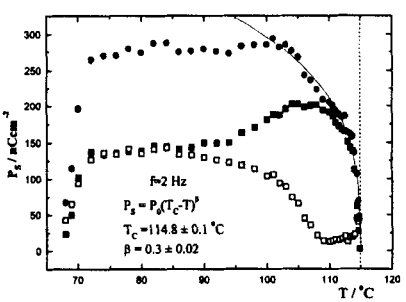


Figure 4 Spontaneous polarization versus temperature for MHP(3F)BBC; ■ - higher peak, - smaller one, ● - sum of both peaks

electric and paraelectric phases the spontaneous polarization should obey the square root law (see Fig.4) with the β parameter equal to 0.5. For the substance under investigation this parameter β is equal to 0.3 what suggests that transition between SmC^* and SmA^* phases seems to be a weak second order.

Dielectric measurements

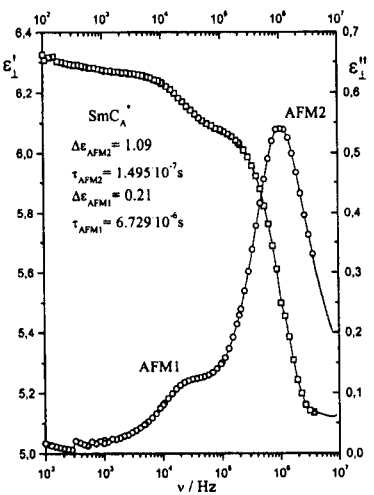


Figure 5 Exemplary dielectric spectrum obtained in antiferroelectric SmC_A^* phase for MHP(3F)BBC

The dielectric relaxation phenomena were studied for paraelectric, ferroelectric and antiferroelectric phases of MHP(3F)BBC using Hewlett Packard analyzer in the frequency range 10 Hz to 13 MHz. Exemplary dielectric spectrum taken in the SmC_A^* for substance studied is presented in Fig.5. As seen in the SmC_A^* antiferroelectric phase two relaxation processes have been observed. The process observed in higher frequency range is more

stronger than that at lower frequencies. This kind of spectrum is characteristic for the antiferroelectric phase and it has been observed by many authors [6-8,11-16]. The sum of two Cole-Cole functions was fitted to the dielectric spectrum of the SmC_A^* phase:

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

where τ_1 and τ_2 are relaxation times, α_1 and α_2 are distribution parameters of the relaxation times, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are dielectric increments for the two processes AFM1 and AFM2 observed in the antiferroelectric phase.

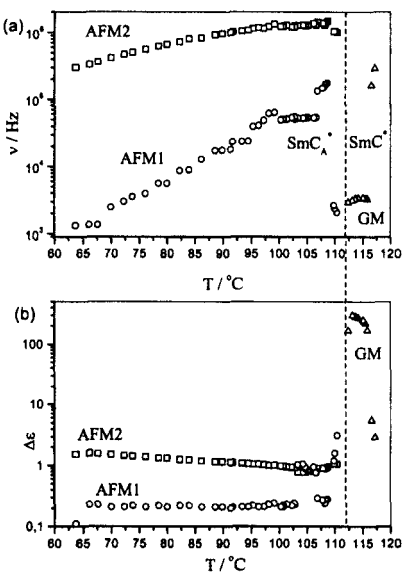


Figure 6 Temperature dependencies of relaxation frequencies (a) and dielectric increments (b) for all modes appearing in the dielectric spectrum of MHP(3F)BBC

Temperature dependence of relaxation frequencies and dielectric increments for all modes observed in dielectric spectrum of MHP(3F)BBC are presented in Fig.6. As one can see in the SmC^* phase a strong Goldstone mode is observed with critical frequency around 3 kHz and dielectric increment of ca. 280. In the antiferroelectric SmC_A^* phase two relaxation processes AFM1 and AFM2 are observed: one

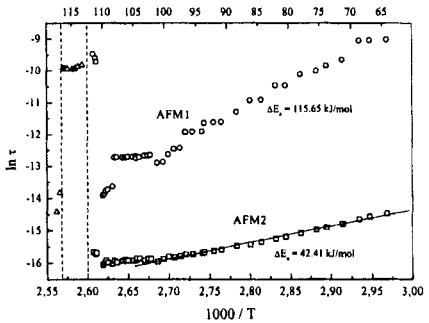


Figure 7 Arrhenius plot for MHP(3F)BBC

showing up at frequency of about several kHz and the second (stronger one) - at frequency of about 1MHz. Considering temperature dependencies of the dielectric increments of these modes one can see that they are almost temperature independent. On the other hand the relaxation frequencies change with temperature. In Fig.7 Arrhenius plots are presented for both modes of the antiferroelectric phase of MHP(3F)BBC. One can see that for the substance under investigation two modes AFM1 and AFM2 with an activation energy equal to 116 kJ/mol and 42 kJ/mol, respectively, have been observed in antiferroelectric SmC_A^* phase. In some papers the processes AFM1 in the lower frequency range is interpreted as reorientation around the short axis (*s*-process). For the substance under investigation the processes with an activation energy equal to 116 kJ/mol could be interpreted as *s*-process. The AFM2 process seems to be the so called non-cancellation mode (NCM). It is interesting that both these processes show Arrhenius behaviour contrary to the results obtained for MHPBBBC [11].

CONCLUSIONS

DSC heating and cooling runs as well as dielectric and electrooptic measurements show reach polymorphism of the substance studied. Using

the current response method two characteristic well-separated peaks for the low temperature range of the antiferroelectric SmC_A^* phase have been revealed. FDDS method shows two relaxation processes in the antiferroelectric SmC_A^* phase: AFM1 denoted as s-process and AFM2 indicated as NCM. Both these processes show Arrhenius type behaviour in the antiferroelectric phase of the substance studied.

ACKNOWLEDGEMENTS

M.M. thanks the Konferenz der deutschen Akademien der Wissenschaften for financial support during her six months stay at the Darmstadt University of Technology. W.H. thanks the Deutsche Forschungsgemeinschaft for finanacial support. A.F. and S.W. thank the State Committee for Scientific Research (KBN) for financial support of this work under grant No. 2P03B 016 17.

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