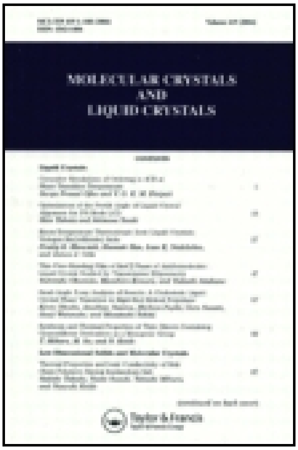

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dielectric and DSC Studies of the Bicomponent Systems with Induced Antiferroelectric Phase Comprising Cyano Terminated Compounds

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Version of record first published: 01 Jun 2009

Mol. Cryst. Liq. Cryst., Vol. 502, pp. 154–163, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902816595

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Phase transitions in pure compounds with cyanoacetyloxyalkoxy groups in terminal chain (2) and second compound comprising alkanoyloxyalkoxy groups (1) and their bicomponent mixture have been studied by optical microscopy, differential scanning calorimetry (DSC) and dielectric spectroscopy. The temperatures, enthalpies of phase transitions and Cp values as a function of temperature were determined for such system by DSC method (Differential Scanning Calorimetry). Dielectric spectroscopy confirmed the presence of induced antiferroelectric phase in mixtures. The Goldstone-mode and the soft-mode relaxation process were observed for SmC phase and also the low frequency P_L and high frequency P_H modes, which are typical for antiferroelectric phase.*

Keywords: cyano compounds; dielectric properties; DSC measurements; induced antiferroelectric phase; liquid crystals

INTRODUCTION

Antiferroelectric materials are very interesting for photonic applications because of their grey scale capabilities, fast electrooptical response and large viewing angle. Many pure compounds also synthesized in our laboratory exhibit the antiferroelectric phase [1–3]. This phase could also be induced in the mixture of compounds with

This work was carried under N20402931/0512 PBS 765 projects.
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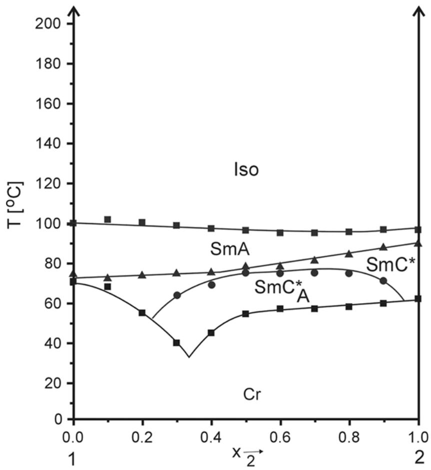


FIGURE 1 The phase diagram of 1–2 system.

only chiral smectic C* phase. The induction and enhancement of antiferroelectric phase were observed for the first time in 2000 when compounds with perfluorinated terminal chain were mixed with compounds with alkyl chain [4,5]. It was shown that there are many systems for which the induced antiferroelectric phase may be formed [4,6,7]. The induced antiferroelectric SmC_A^* phase in bicomponent mixtures comprising compounds with cyano groups in terminal chain and compounds with alkyl group was discovered recently by testing the phase diagrams of their mixtures [6–8]. The system 1–2 (Fig. 1) was chosen for the careful studies by different methods- thermomicroscopic, electrooptical and X-ray measurements [9]. The temperatures and enthalpies of phase transitions and function of temperature were determined for such systems by DSC method. Dielectric spectroscopy is a very useful experimental method for characterization of liquid crystal phases [11] and gives us possibility to review the phase situation in the system 1–2.

EXPERIMENTAL

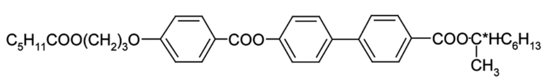
Phase transition temperatures were studied by an observation of the light transition through the measuring cell placed in the birefractive system. The measuring setup consisted of a polarizing microscope (BIOLAR PI) with a halogen lamp powered with a stabilised power supplier, rotating heating hot stage (LINKAM – THMS-600) and silicone photo detector (FLC PIN 20). The rate of temperature change was 1 deg/min near the phase transition region. Phase transitions temperatures versus concentration in mole ratio are presented on phase diagrams. The temperatures of phase transitions and enthalpies were measured by means of a DSC 141 Setaram calorimeter. The measurements were made in the both heating and cooling cycles, at the rate of 1 deg/min. A sealed crucibles with the sample were heated to the isotropization temperature of the sample. After this procedure the DSC measurements were started.

The cells with golden electrodes prepared in the laboratory of the Institute of Physics in MUT, planar orientation inside the cell was used for complex dielectric permittivity measurements using HP 4192A impedance analyser. The cell temperature was controlled by a THS 92 Linkam heater. The heating and cooling rate was 0.1°C/min. The automatic data acquisition arragement was made using RS 232 interfacing with a PC. Measurements were made in the frequency range 5 Hz–13 MHz. A DC bias field of 1 V/μm was used to suppress the Goldstone-mode.

RESULTS

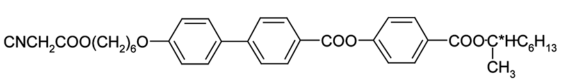
It was shown that there are many systems for which the induced antiferroelectric phase may be formed [4,6,7]. The results of DSC and dielectric measurements of induced antiferroelectric SmC_A^* phase in bicomponent mixtures comprising compounds with cyano groups in terminal chain and second compound comprising alkyl group is presented below. The preparation of the compounds used in the present work has been described in Ref. [3,10]. Molecular structures and the observed under polarizing microscope phase sequences (during heating) are presented below:

Compound 1



Cr 71.3 SmC* 75,2 SmA 101,1 Iso

Compound 2



Cr 62.2 SmC* 90.5 SmA 97.6 Iso

Both of the compounds presented above are S enatiomers and their preparation is described in Ref. [3,10].

The bicomponent mixtures of system 1–2 were chosen for careful study by different methods- thermomicroscopic, electrooptical and X-ray investigation have been made until now [9].

The reviewed phase diagram is presented in Figure 1. Firstly we supposed that the phase transition SmC$^*_\gamma$-SmC$^*_A$ appears, which is difficult to notice using a polarizing microscope [6–9]. The antiferroelectric phase is observed under a polarizing microscope in concentration ranging from 0.3 to 0.9 mole fraction of compound 2, but DSC measurements showed that it phenomena existed also in a concentration of 0.2 mole fraction of compound 2. We observed that the phase transition SmC*-SmC$^*_A$ in concentration lower than 0.5 mole fraction of compound 2 looked completely different under the microscope than in higher concentrations. It was suggested that maybe SmC$^*_\gamma$ is present in the system 1–2. We did not observe the SmC$^*_\alpha$-SmA phase transition under the polarizing microscope.

The DSC measurements confirmed phase transitions and also the existence of two different subphases of the SmC* phase, Figures 2 and 3. We observed the SmC$^*_A$-SmC* phase transition in concentrations ranging from 0.2 to 0.9 mole fraction of compound 2 and a first order transition to SmA in the heating stage. The DSC measurements of pure compound 1 showed two phase transitions, SmA-SmC$^*_\alpha$ and SmC$^*_\alpha$-SmC*, in cooling stage, shown in Figure 3. The enthalpy of these phase transitions is very small and firstly we supposed that

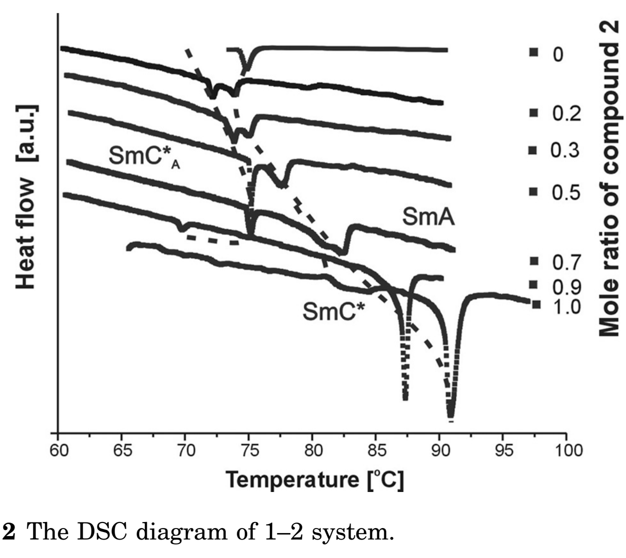


FIGURE 2 The DSC diagram of 1–2 system.

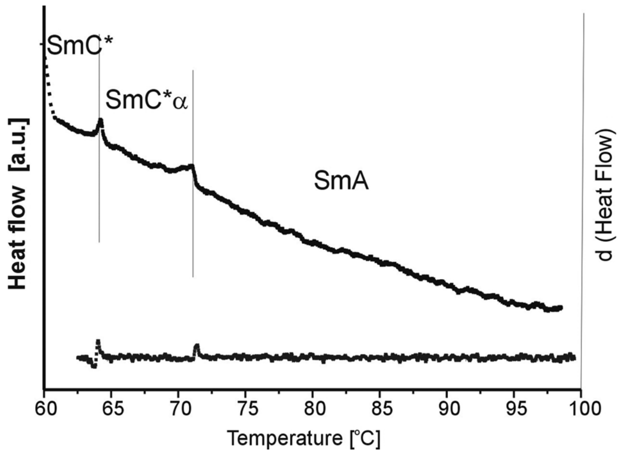


FIGURE 3 The DSC diagram of pure compound 1.

the SmC*-SmC_{γ}^{*} phase transition was possibly present, but calculation of dheat flow/dt showed us only two phase transitions Figure 3.

The real parts of dielectric permittivity for pure compound 1 are presented in Figure 4. The Iso-SmA phase transition was observed near 104°C. The SmC_{α}^{*} subphase appeared at 73°C and the SmC* phase is observed in the temperature range 71–65°C. It is possible that SmC_{γ}^{*} exists at temperatures below 65°C but molecular crystals appeared very fast. The relaxation frequencies were calculated from the Cole-Cole plots, Figure 5. Typical soft mode was detected for the SmA phase and the highest value of frequency mode was 400 kHz. When temperature is decreasing, the relaxation frequency goes down to 20 kHz in the SmC_{α}^{*} phase. In the SmC* and SmC_{α}^{*} phases we also

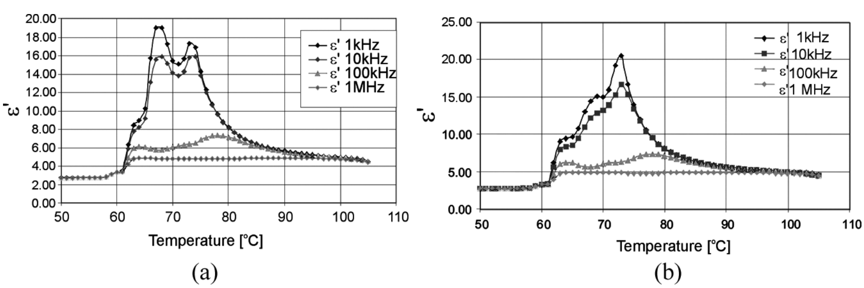


FIGURE 4 Temperature dependence of real part of dielectric permittivity for four different frequencies of compound 1, (a) without bias field and (b) with bias field 1 V/μm.

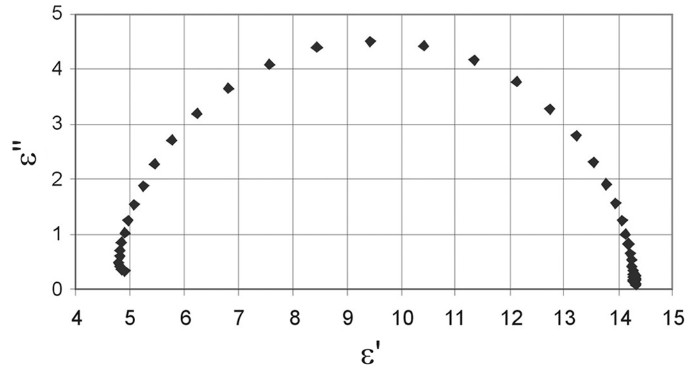


FIGURE 5 Cole-Cole plot for SmC* phase (75°C) of compound 1. Goldstone mode is detected.

detected the Goldstone mode, Figure 5. The relaxation frequency of Goldstone mode is around 15–25 kHz. We did not detect any modes at temperatures below 65°C, in pure compound 1.

The real part of dielectric permittivity for the mixture containing 0.3 mole fraction of compound 2 is presented in Figure 6. The SmC^*_α subphase appeared at 82°C and the SmC* phase is observed in the temperature range 75–78°C. The induced antiferroelectric phase appeared below 75°C. The temperature range of SmC^*_A was very broad, around 30°C. The relaxation frequencies were calculated from the Cole-Cole plots, Figure 7. Typical soft mode was detected for the SmA phase and the highest value of frequency was 10 MHz, the lowest 10 kHz. When temperature is decreasing, the relaxation frequency goes down to the SmC^*_α phase. In the SmC* phase the Goldstone mode was noticed and the relaxation frequency of mode is around 10 kHz.

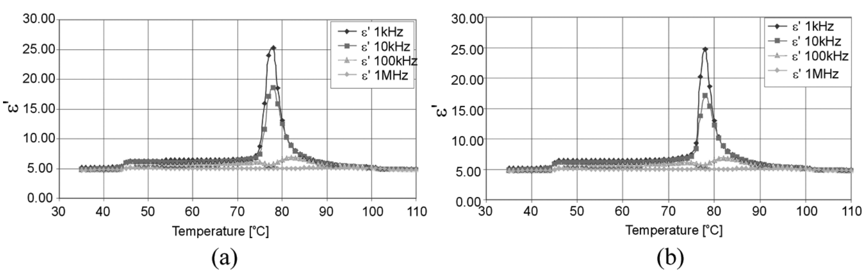


FIGURE 6 Temperature dependence of real part of dielectric permittivity for four different frequencies of mixture containing 0.3 mole fraction of compound 2, (a) without bias field and (b) with bias field 1 V/μm.

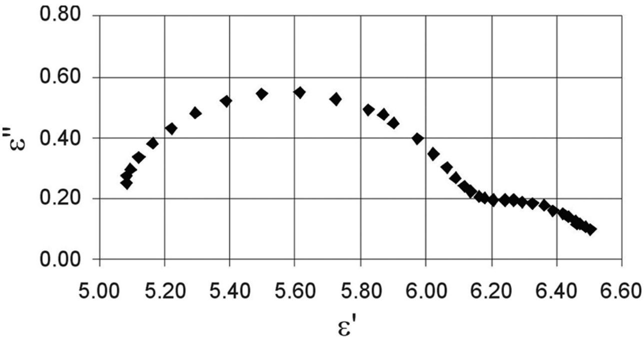


FIGURE 7 Cole-Cole plot for SmC_A^* phase (60°C) of mixture containing 0.3 mole fraction of compound 2. Two modes (P_H, P_L) are visible.

The typical modes P_L and P_H for the antiferroelectric phase were detected in temperatures below 75°C, Figure 7. The P_H-mode relaxation frequency was around 200–300 kHz and at lower temperatures the a relaxation frequency of the second P_L-mode decreases.

In the SmA phase soft mode was detected and the relaxation frequency was between 10 MHz and 10 kHz (the relaxation frequency decreases with temperature) in a mixture of 0.5 mole fraction of compound 2. The SmC_α^* subphase was noticed at temperatures ranging from 80° to 78°C and below this temperature the SmC* phase was noticed, Figure 8. The relaxation frequency of the Goldstone mode was around 10 kHz. The induced antiferroelectric phase occurred within the temperature range 75–45°C. The relaxation frequencies were calculated from the Cole-Cole plots, Figure 9. The typical modes

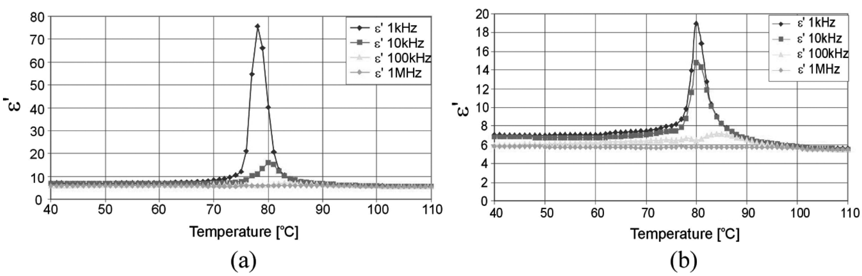


FIGURE 8 Temperature dependence of real part of dielectric permittivity for four different frequencies of mixture containing 0.5 mole fraction of compound 2, (a) without bias field and (b) with bias field 1 V/μm.

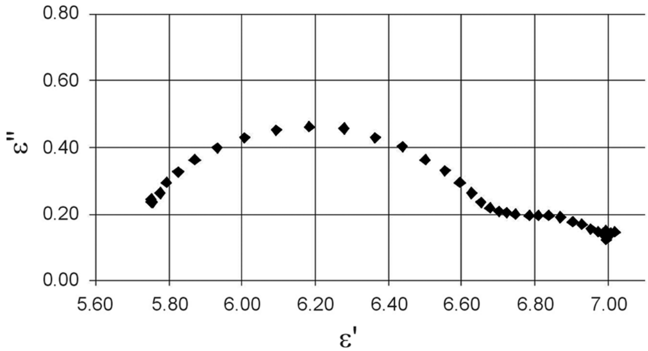


FIGURE 9 Cole-Cole plot for SmC_A^* phase (58°C) of mixture containing 0.5 mole fraction of compound 2.

P_L and P_H for antiferroelectric phase were detected in temperatures below 75°C. The P_H-mode relaxation frequency was around 50–200 kHz and the P_L-mode was lower than 2 kHz. A similar situation was observed for the mixture containing 0.7 mole fraction of compound 2.

The SmA phase was detected in the temperature range 108–96°C in a mixture of 0.9 mole fraction of compound 2, Figure 10. Soft mode was detected in this phase and the relaxation ranged frequency ranged from 4 MHz to 10 kHz. The SmC_α^* subphase was noticed around 96–93°C and below this temperature the SmC^* phase was present in a very broad range of temperatures (93–20°C). The relaxation frequency of Goldstone mode was observed to be around 0.4–0.1 kHz,

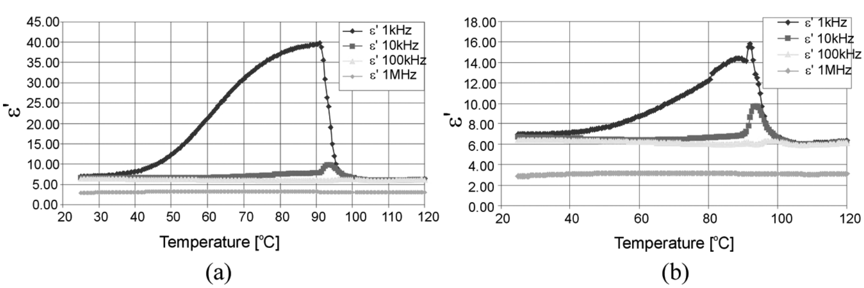


FIGURE 10 Temperature dependence of real part of dielectric permittivity for four different frequencies of mixture containing 0.9 mole fraction of compound 2, (a) without bias field and (b) with bias field 1 V/μm.

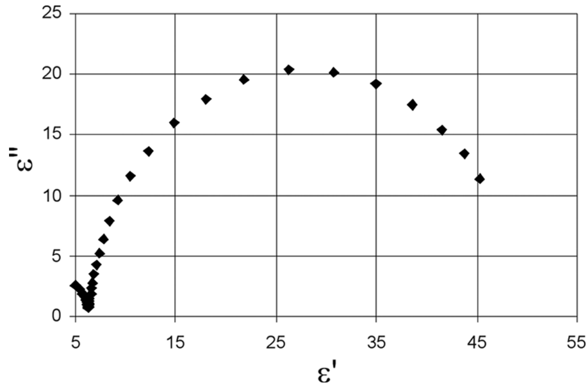


FIGURE 11 Cole-Cole plot for SmC* phase (50°C) of mixture containing 0.9 mole fraction of compound 2. Goldstone mode is detected.

Figure 11. The typical modes P_L and P_H for the antiferroelectric phase were not detected at any temperature.

The SmA phase was detected in the temperature range 101–87°C of pure compound 2, Figure 12. Soft-mode was detected in this phase and the relaxation frequency was observed to range from 4 MHz to 10 kHz. The SmC^*_α subphase was noticed at around 87°C and below this temperature the SmC* phase was present in a very broad range of temperatures (85–50°C). The relaxation frequency of the Goldstone mode was around 0.4–0.1 kHz. The relaxation frequencies were calculated from the Cole-Cole plots, Figure 13. The typical modes P_L and P_H for the antiferroelectric phase were not detected at any temperature, for compound 2.

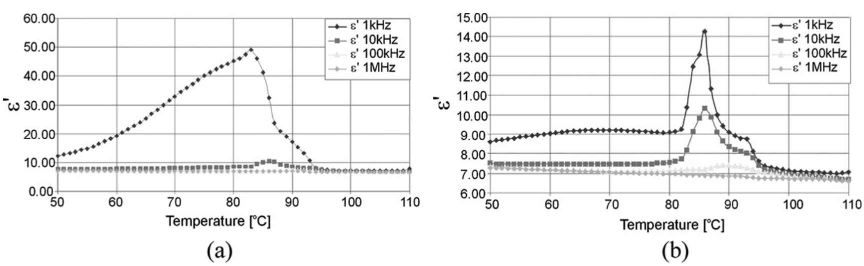


FIGURE 12 Temperature dependence of real part of dielectric permittivity for four different frequencies of compound 2, (a) without bias field and (b) with bias field 1 V/μm.

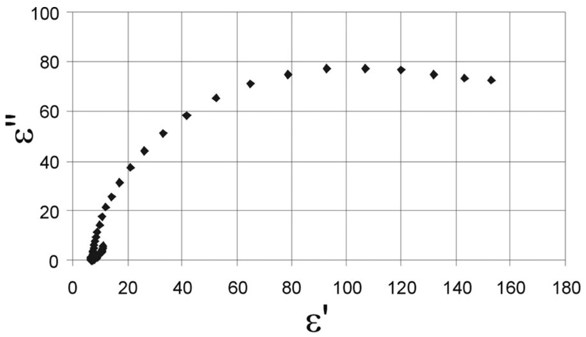


FIGURE 13 Cole-Cole plot for SmC* phase (80°C) of compound 2. Strong Goldstone mode is visible.

CONCLUSIONS

The induced antiferroelectric smectic phase was confirmed for the mixtures of two compounds: one with alkyl terminal chain and another with cyano terminal group. The concentration range of the induced antiferrolectric phase is 0.3 to 0.7 mole fraction of compound 2. The DSC measurements evidenced the phase transitions Cr-SmC_A^*-SmC^*-SmC_α^*-SmA-Iso. Dielectric spectroscopy confirmed the phase situation for investigated bicomponent mixtures of compounds 1 and 2 and both pure compounds.

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