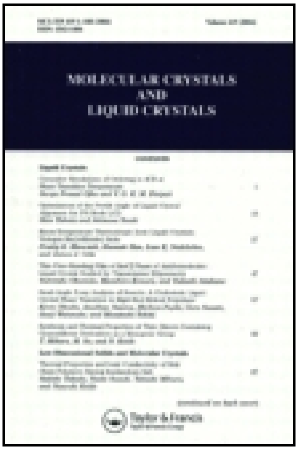

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Helical Pitch in Bicomponent Mixtures with Induced Antiferroelectric Phase

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The induced antiferroelectric phase in bicomponent mixtures of fluorinated compound $C_6F_{13}C_2H_4OPhPhCOOPhCOOC^*H(CH_3)C_6H_{13}$ and a member of homologous series of $C_nH_{2n+1}COO(CH_2)_3OPhCOOPhPhCOOC^*H(CH_3)C_6H_{13}$ (n = 1-7) are observed. In those systems also SmC^*_α phase was evidenced. The helical pitch was measured and it was found that helical pitch increases with the increase of concentration of fluorinated component in mixture. The pitch of SmC^*_A phase is longer than for SmC^* phase. Additionally the pitch in induced SmC^*_A phase does not depend on temperature, while in single compounds with SmC^*_A phase strongly increases.

Keywords: antiferroelectric phase; ferroelectric phase; helical pitch; induction of phase

INTRODUCTION

Chiral anticlinic phase SmC^*_A (antiferroelectric phase) can be induced in the mixture composed only of chiral synclinic compounds (ferroelectric phase – SmC^*). Several such systems were described recently [1]. It broadens the range of compounds useful for preparation of antiferroelectric mixtures for display application. New bicomponent systems with induced antiferroelectric phase, giving the possibility to test influence of the chain length on induced ability, are presented here. The fluorinated compound (1) giving the induction of antiferroelectric

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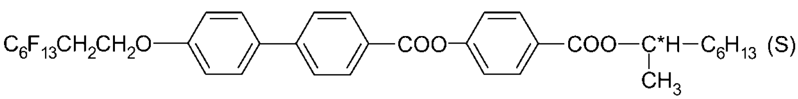
phase is the same as in previous papers [1,2]. But it was mixed with newly synthesised members of homologous series (2) having only smectic A or smectic C* phase [3].

The helical pitch measurements of antiferroelectric materials, synthesised by us, show the strong dependence on temperature [4,5]. The helical pitch is short (about 400–600 nm) in room temperature and increases with increasing temperature. It was interesting to test the helical pitch in induced antiferroelectric phase ands its temperature dependence. The pitch measurements were performed for two bicomponent systems.

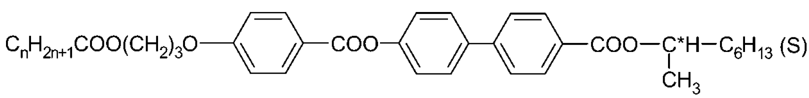
EXPERIMENT

The chiral fluorinated compound of the following structure and phase transitions:



(1)

Cr_1 80.7 Cr_2 98.1 SmC* 138.0 SmC_α^* 148.1 SmA 183.6 Iso
was mixed with a member of homologous series (n = 1-7) of the following structure:



(2)

2a n = 1 Cr 72.3 SmA 104.3 Iso
2b n = 2 Cr 80.6 SmA 106.7 Iso
2c n = 3 Cr 109.9 (SmA 107.1) Iso
2d n = 4 Cr 111.9 (SmA 104.8) Iso
2e n = 5 Cr 71.3 SmC* 75.2 SmA 101.1 Iso
2f n = 6 Cr 71.4 SmC* 75.1 SmA 97.1 Iso
2g n = 7 Cr 67.2 SmC_γ^* 73.2 SmC_β^* 76.6 SmC_α^* 78.2 SmA 95.7 Iso

Compounds 2 have phase sequence SmA-Iso (2a-d) or SmC*-SmA-Iso (2e-g). When they are added to compound 1, which phase sequence is SmC*-SmC_α^*-SmA-Iso, the induction of antiferroelectric phase occurs.

The phase diagrams were constructed based on the single concentration method. The phase transition temperatures were measured based on the polarizing thermomicroscopic method. The microscope BIOLAR, equipped with the heating stage LINKAM THMS 600, was

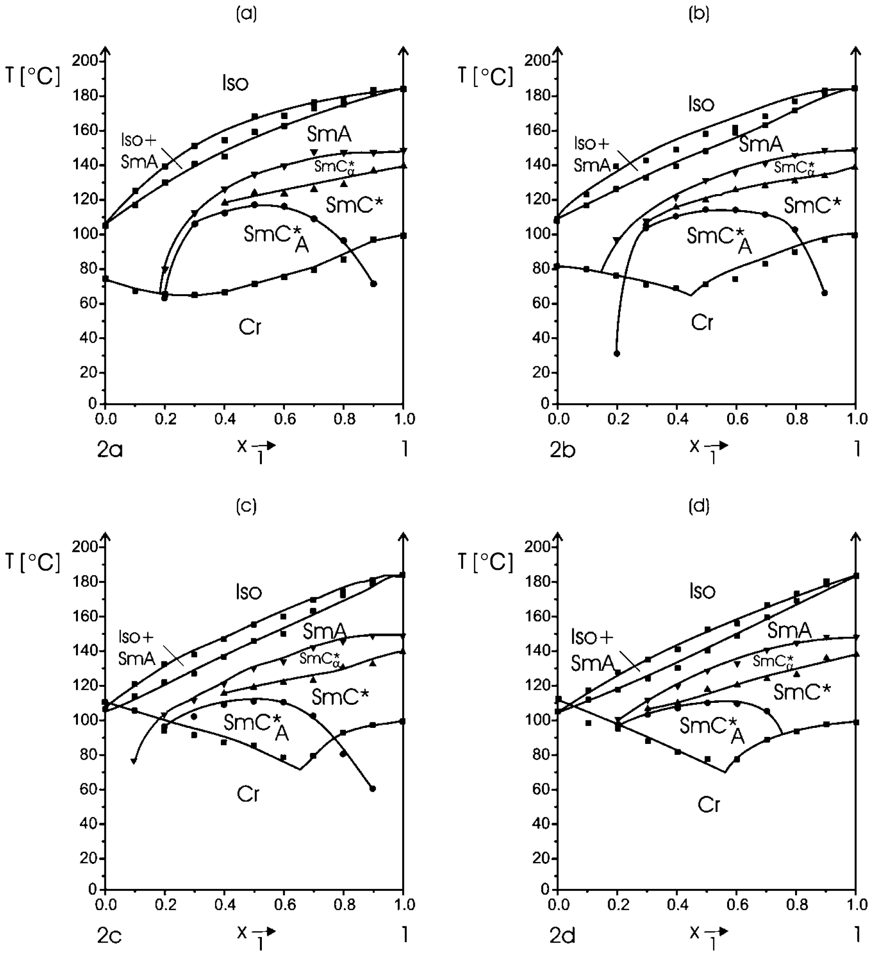


FIGURE 1 The phase diagrams of the bicomponent systems 1-2 (n = 1–7).

used. The accuracy of temperature setting 0.1°. The heating rate 1°/min.

The helical pitch measurements were made based on the selective light reflection phenomenon. The measurements of light transmission were made on Varian Cary 3 UV-vis spectrometer in the range of 400–900 nm. The tested compounds were placed on glass plate with homeotropic aligning layer without covering with another glass plate. Temperature was changed with the use of thermocontroller UNIPAN 600. The temperature accuracy was 0.1°; temperature range from room temperature to 160°C.

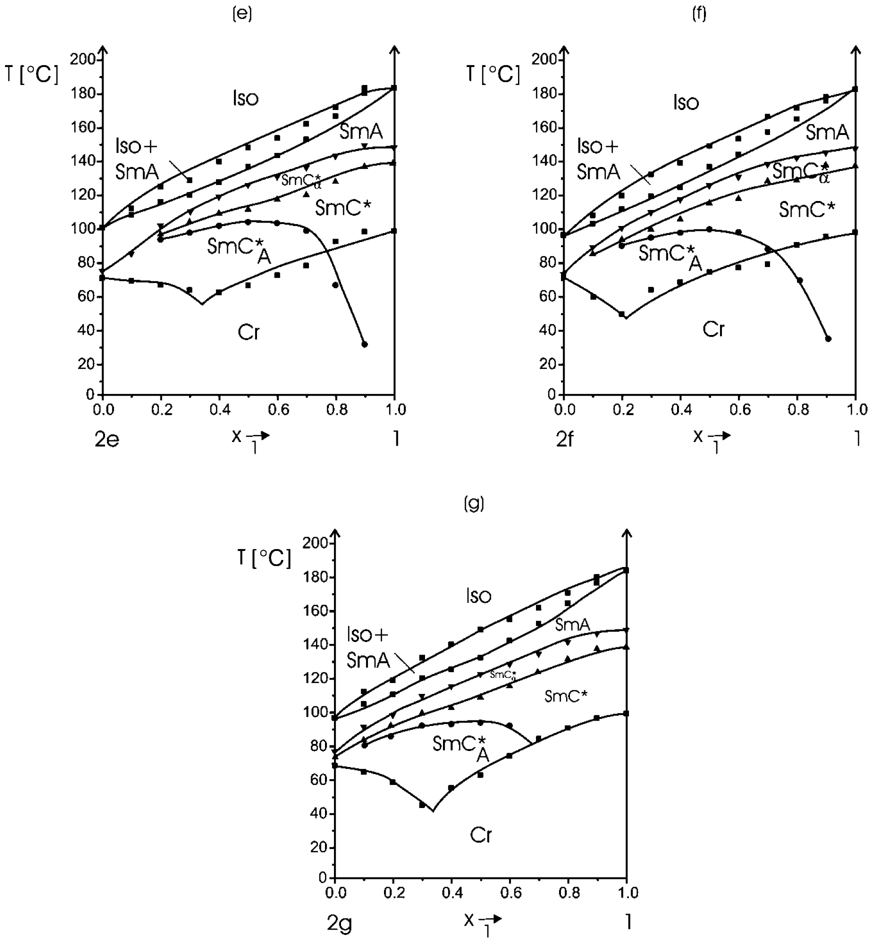


FIGURE 1 Continued.

The results are presented as the maximum wavelength of selectively reflected light versus temperature on all figures. The helical pitch length is obtained dividing the values of wavelength by 1.5 (the value of average refractive index for this class of materials [6]).

RESULTS

Phase Transition Measurements

The phase diagrams of the bicomponent systems 1-2 (n = 1–7) are presented in Figure 1a-g.

In the all diagrams the induced antiferroelectric phase is observed. The narrower concentration range of its existence is for short homologues (from 0.3 to 0.9 mole ratio for 2a-1) and broader for longer homologues (from 0.2 to 0.9 mole ratio for 2f-1). For mixtures with longer chain the transition between SmC^* and SmC^*_A phase is not seen well in the concentration range of big excess of compound 2.

When a member from the homologous series 2 (2a-2d) does not exhibit tilted smectic phase (SmC^* or its subphases) this phase is destabilized in the mixture. Members from the homologous series 2 (2e-2g) exhibiting tilted smectic phase (SmC^* or its subphases) which mixes additively with smectic phase of compound 1.

In the all phase diagrams the phase transition between phase SmC^*_α and SmC^* is well seen up to concentration range where SmC^*_A phase reach maximum stability. We have not determined exactly the kind of subphases in binary mixtures, except for compounds 1 [7] and 2 g [8].

Helical Pitch Measurements

For systems 2a-1 and 2g-1 (Fig. 1a, g) the helical pitch measurements were performed and their results are presented in Figures 2, and 3, respectively.

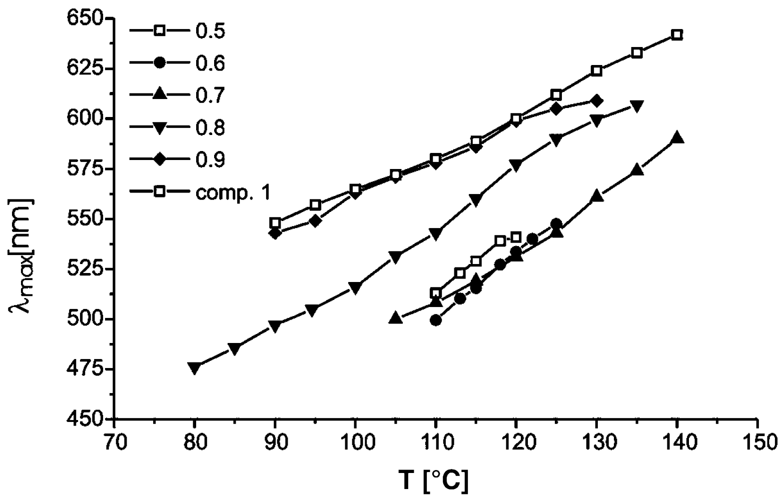


FIGURE 2 The maxima of selectively reflected light versus temperature for the system 2a-1.

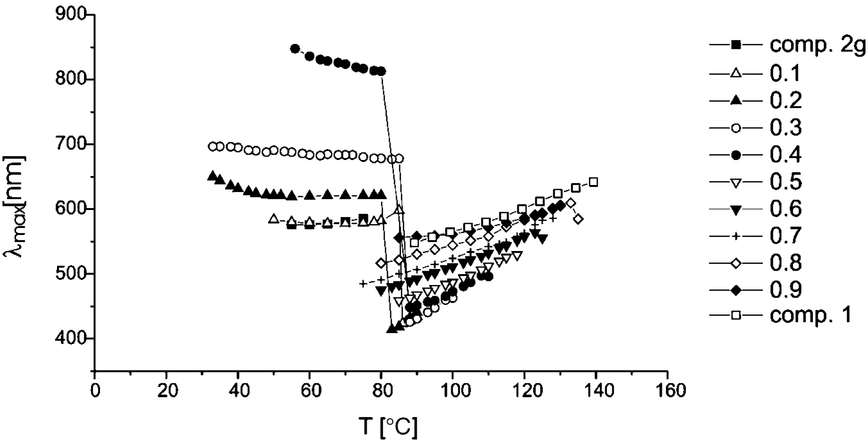


FIGURE 3 The maxima of selectively reflected light versus temperature for the system 2g-1.

Concerning the system 2g-1 (Fig. 3) it is seen that the selective reflection was measured in CmC* and SmC_A^* phases. SmC_α^* has very short pitch and it is not possible to measure it. The helical pitch of SmC* phase is shorter than for SmC_A^* phase. The jump in maximum wavelengths of selectively reflected light is observed crossing the phase transition from SmC* to SmC_A^* phase. The values of helical pitch of SmC* phase decrease with decreasing the concentration of compound 1 up to 0.1 mole ratio. Single compound 2g exhibit SmC_γ^* phase in lower temperatures below SmC_α^* [8]. The values of helical pitch of compound 2g in phase SmC_γ^* is comparable with values obtained for induced antiferroelectric phase (small concentration of compound 1 (0.1 mole ratio)). The areas of induced SmC_A^* is not symmetrical to both components. It is shifted to higher concentration of compound 2. It suggests stronger ability for induction of the compound 2g than 1. The helical pitch of SmC_A^* phase increases with increasing the concentration of compound 1. Unfortunately the results for concentrations higher than 0.4 mole ratio of compound 1 are out of the range of spectrophotometer. What is worth to notice is that the temperature dependence of helical pitch in induced antiferroelectric phase is constant, contrary to the results obtained for single antiferroelectric compounds [5,9].

For the system 2a-1 (Fig. 2) the results of helical pitch measurements are similar to the above described. There are also no results for SmC_α^* phase. The helical pitch in SmC* also decreases with the decrease of concentration of fluorinated compound 1. In induced antiferroelectric phase the pitch is higher than in SmC* phase, but it was not measured because in the whole concentration range of existence of induced antiferroelectric phase the pitch was out of the spectrophotometer range. Thus the pitch in antiferroelectric phase seems to be very long.

CONCLUSIONS

New systems with the induction of antiferroelectric phase in mixtures of compounds exhibiting SmC* or SmA phase are presented. The temperature-concentration area of induced SmC^*_A phase is not symmetrical in relation to concentration of components mole ratio 1:1. In all systems also the SmC^*_α phase exists, observed in compound 1.

The results of helical pitch measurements performed for two systems 1-2a and 1-2g show that helical pitch increases with the increase of concentration of fluorinated compound both in SmC* and SmC^*_A phases, and that the pitch of induced SmC^*_A phase is longer than for SmC* phase. Additionally the pitch in induced SmC^*_A phase for 1-2g does not depend on temperature and for 1-2a is probably long.

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