A smectic C*-smectic A tricritical point in a mixture of two compounds exhibiting high spontaneous polarization

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X-ray diffraction, D.S.C. and miscibility studies have been performed on binary mixtures whose constituent compounds exhibit large values of spontaneous polarization. These studies have led to the observation of a tricritical point for the smectic C*–smectic A transition. The origin of this tricritical behaviour is discussed in relation to the range of the smectic A phase and the large spontaneous polarization.

1. Introduction

The smectic C–smectic A (or S_C–S_A) as well as smectic C*–smectic A (or S_C^*–S_A) transitions are generally observed to be second order. However, recently ferroelectric materials exhibiting large spontaneous polarization, e.g. 4-(3-methyl-2-chloropenta-noyloxy)-4′-heptyloxybiphenyl or C7 and 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl or A7 have been shown to exhibit first order S_C^*–S_A transitions [1–3]. It has also been shown [2] that adding a non-chiral compound to C7 drives the transition towards second order and hence towards a tricritical point. Detailed X-ray studies have provided clear evidence of a mean field to tricritical crossover behaviour near this mean field tricritical point [4]. High resolution specific heat investigations [3] have also yielded a very interesting result: although A7 exhibits a first order S_C^*–S_A transition, its racemate shows a second order transition, this transition being *at* a mean field tricritical point.

The origin of the first order nature of the S_C^*–S_A transition in C7 and A7 is of considerable interest. Although it is expected [5] that the temperature range of the smectic A phase should play an important role, it is not clear if this is entirely the case. For instance, both C7 and A7 have nearly the same temperature range for the smectic A phase (about 8–10°C). But the S_C^*–S_A transition of A7 has a transition enthalpy which is about a factor of two less than that of C7. Considering that the spontaneous polarization (P_s) of A7 is also about 50 per cent less than that of C7 [1], it is conceivable that the large value of P_s might also influence the nature of the S_C^*–S_A transition. The results on A7 and its racemate [3] as well as on mixtures involving C7 and a non-chiral compound [2] also indicate the same behaviour.

In this paper we present the results of our studies on binary mixtures of two ferroelectric liquid crystals *both* of which exhibit large P_s. These results show that the S_C^*–S_A transition can be second order despite the large P_s values.

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2. Experimental

The compounds, which are hereafter abbreviated as 2*f* and 3*f*, are both chiral esters of 2,5-diphenyl pyrimidines [6]. Their structural formulae are shown in figure 1. The compound 3*f* forms smectic A and C* phases while 2*f* shows S_C^* in addition to two other higher order smectic phases.
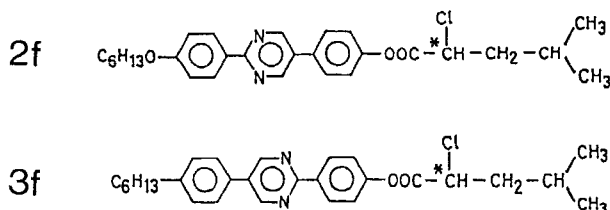

Figure 1. Chemical formulae of the compounds 2*f* and 3*f*.

The polarization data were obtained by using the Diamont bridge technique. The D.S.C. studies were done by using a Perkin–Elmer DSC-4 with TADS while the X-ray investigations have been carried out using a computer controlled Guinier diffracto-meter (Huber 644). The details of the experimental techniques have already been published [7, 8] and will not be repeated here.

3. Results and discussion

The variations of P_s for 2*f* and 3*f* are shown in figure 2. It is seen that both materials show large P_s values. The mixtures of 2*f* and 3*f* are also expected therefore to have a large P_s. It is also evident from the figure that the variation of P_s is steeper for 3*f* than for 2*f*, presumably because the latter material exhibits a direct smectic C*–isotropic transition while the former exhibits a S_C^*–S_A transition.

Figure 3 shows the phase diagram for the 2*f*–3*f* binary system. It is seen that addition of 2*f* initially increases (or decreases) the range of the S_A (or S_C^*) phase. But with a further increase in the concentration of 2*f* in the mixture, the S_A range decreases drastically until finally for a concentration of about 90 mol per cent the S_A phase is completely suppressed. Thus, we have here a binary system with a large P_s and with a widely varying temperature range. It is of interest to see how these factors affect the nature of the S_C^*–S_A transition.
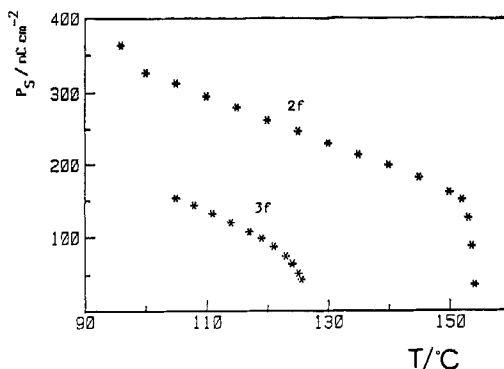

Figure 2. Variation of the spontaneous polarization (P_s) with temperature in the smectic C* phase of 2*f* and 3*f*. The data at the highest temperatures for 2*f* are affected by the smectic C*–isotropic two-phase region and hence are not reliable.
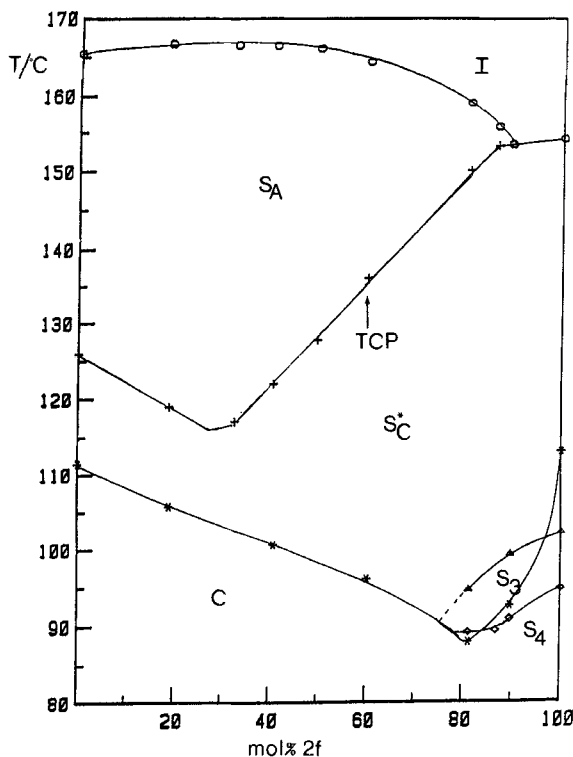
Figure 3.   Phase diagram of $2f$–$3f$ mixtures.

A combination of D.S.C. and X-ray diffraction studies have been performed on $3f$ as well as on two binary mixtures of $2f$ in $3f$ whose concentrations (expressed in mol % of $2f$) are 58·27 and 60·20. The results on $3f$ (not shown here) indicated that the S_C^*–S_A transition in this material is second order. Figure 3 shows the results of the D.S.C. investigations on the 58·27 and 60·2 mixtures. For both concentrations the D.S.C. runs have been taken for the S_C^*–S_A transition at four different heating rates, viz, 0·1, 0·3, 0·5 and 1·0°C/min. The total area under the peak was computed. This gives ΔH, the enthalpy including both latent heat and specific heat contributions. The plot of ΔH versus heating rate is shown in figure 4. It is observed that ΔH decreases only slightly with decreasing heating rate for the 60·2 mixture while it decreases steeply for the 58·27 mixture. A linear extrapolation to zero heating rate yields, to a good approximation, the latent heat $(\Delta H)_0$ of the transition [8]. The values of ΔH_0 evaluated in this manner for the 58·27 and 60·2 mixtures are 0·16 J/g and 0 J/g respectively. It can be concluded therefore that the S_C^*–S_A transition for the 60·2 mixture is first order while that for the 58·27 mixture is second order, there being a tricritical point for intermediate mixtures. This conclusion is also supported by the X-ray results (see figures 5 and 6). For the 60·2 mixture there is a coexistence region in which the density modulations corresponding to both the S_C^* and S_A phases can be seen. Also, the layer spacing, d, exhibits a jump of about 0·8 Å. These results signify, as for C7 and its mixtures studied earlier [2], a first order transition. On the other hand the layer spacing for the 58·27 mixture does not show a jump and no coexistence region is observed either, showing thereby that the S_C^*–S_A transition is second order. Hence it can be concluded that there exists a tricritical
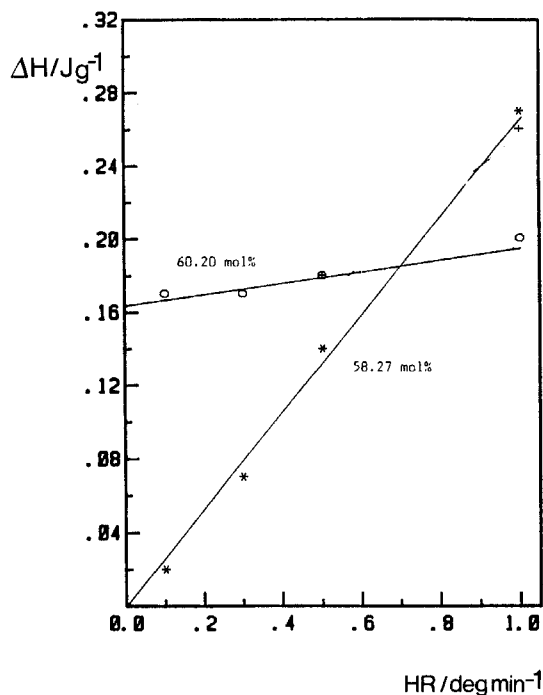
Figure 4.   Variation of the total enthalpy associated with the S_C^*–S_A transition versus the heating rate for mol % $2f$ in $3f$. The enthalpy extrapolated to zero heating rate gives the transition enthalpy (see text).
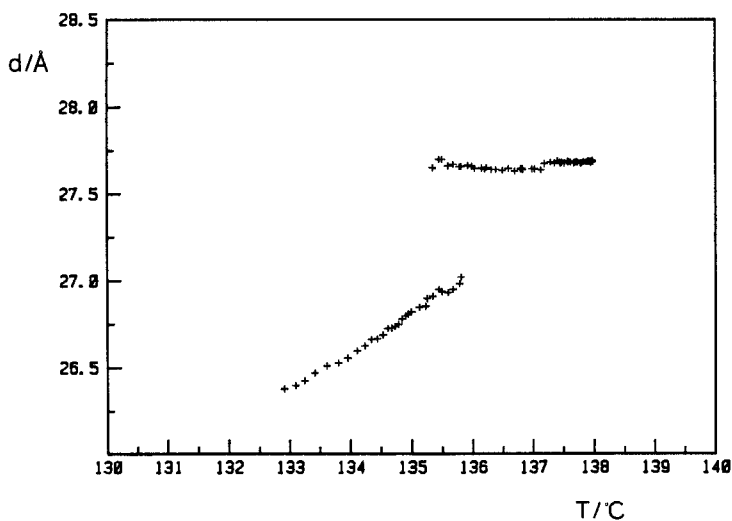

Figure 5.   Variation of the layer spacing, d, with temperature in the smectic C* and A phases of the 60·2 mixture.

point for the S_C^*–S_A transition for $2f$–$3f$ mixtures in the concentration range of 58·27 and 60·2.

Generally, smectic C–smectic A as well as smectic C*–smectic A transitions are second order. The only exceptions so far are the materials A7 and C7 in which a first
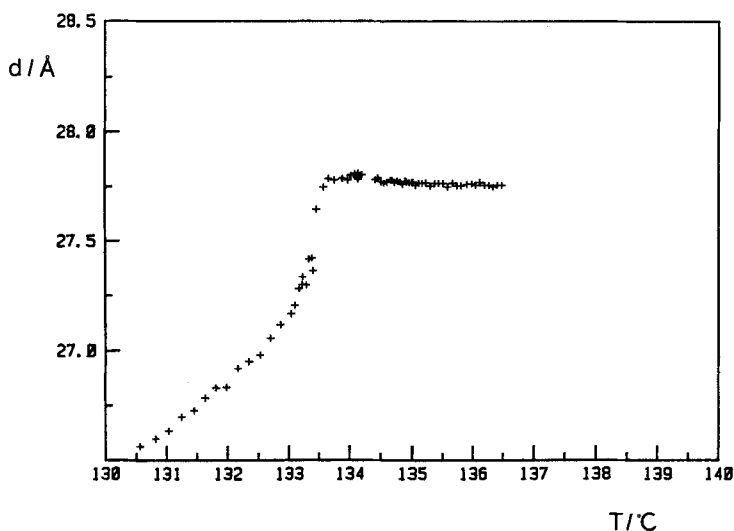
Figure 6.   Temperature variation of the layer spacing d in the smectic C* and A phases of the 58·27 mixture.

order S_C^*–S_A transition has been observed. Considering that both these materials have a large value of P_s, it is possible to expect that the large P_s may be *one* of the factors which are driving the transition to be first order. On the other hand, the present studies have shown the S_C^*–S_A transition can be second order even in materials which exhibit a large value of spontaneous polarization showing thereby that the magnitude of P_s is *not the only factor* that determines the order of this transition. As regards the influence of the range of the smectic A phase, the present results have shown that the S_C^*–S_A transition is first order even when the range of the S_A phase is as large as 28°C. It can be recalled that materials with much smaller smectic A ranges show only second order S_C–S_A or S_C^*–S_A transitions [5]. It is, of course, possible that *both* spontaneous polarization and the smectic A range may influence the nature of the transition, although the relative roles of these factors is uncertain. Clearly, further studies are required to understand the S_C^*–S_A transition.

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