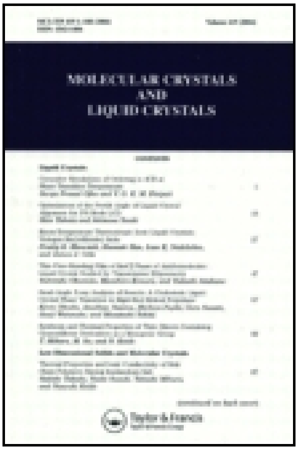

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The Influence of Chirality on the Phase Behaviour of a Fluoro-Substituted Tolan Derivative Exhibiting a Direct TGB to BP Transition

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We have investigated the phase behaviour as a function of enantiomeric excess of a fluoro-substituted tolan derivative, FH/FH/HH18BTMHC, using high-resolution adiabatic scanning calorimetry (ASC). This substance exhibits a direct TGB to BP transition. Mixing (R) and (S) enantiomers permits us to vary the chirality of these mixtures without much effect on other parameters. Changes in transition temperature are studied, as well as the enthalpy changes and latent heats at the various transitions which can be measured directly using ASC. A supercritical BPIII-I transition evolving towards a critical point is observed.

Keywords: phase transitions; chirality; TGB; Blue phases

INTRODUCTION

Chirality gives rise to a number of specific phases, like chiral nematic (N*), chiral smectic C (S_{C^*}), twist grain boundary (TGB) and blue phases (BP). The sample we have investigated is a fluoro-substituted tolan derivative, (R) or (S)-1-methylheptyl 3'-fluoro-4'-(3 fluoro-4-octadecyloxybenzoyloxy) tolane-4-carboxylate, abbreviated as FH/FH/HH18BTMHC. This compound was prepared and examined by the Bordeaux group. Opposed to previous experimental observations of liquid crystals with both TGB and blue phases, this substance exhibited a direct TGB to BP transition without an intermediate N* phase [1,2]. The phase sequence of the pure (R) compound is S_{C^*}-TGB_C-TGB_A-BPI-BPII-BPIII-I. DSC scans showed the occurence of BPII only on cooling [2] but high resolution ASC scans on this pure compound [3] clearly showed the presence of BPII also on heating. Furthermore they clearly confirmed that the BPIII-to-isotropic C_p peak did not represent a real transition but merely a supercritical C_p increase. A further investigation of the effect of enantiomeric excess on phase behaviour and phase transitions in this system is the subject of this paper. Mixing (R) and (S) enantiomers has the advantage that it enables us to vary the chirality with only a small effect on other parameters due to diastereomeric interactions. The evolution of the BPIII-I supercritical peak towards a critical point, in analogy with liquid-gas systems[4], was closely monitored.

EXPERIMENTAL METHOD

Adiabatic scanning calorimetry (ASC) is a well established high resolution calorimetric technique which is particulary useful for studying the nature of a phase transitions, because of its ability todirectly measure the enthalpy, thus being able to distinguish the actual latent heat ΔH_L from pretransitional enthalpy increases δH, even for weakly first-order transitions. The ASC calorimeter has different stages. Stage 1 contains the investigated sample inclosed in a holder. Its heat capacity C_1 is the sum of the contributions C_h of the holder and C_s of the sample

$$C_1 = C_s + C_h = \frac{P_1}{\dot{T}_1}$$

where T_1 is the temperature of stage 1, $\dot{T}_1 \equiv dT_1 / dt$ is obtained by numerical differentiation of $T_1(t)$ data as a function of time, and $P_1 = P_1^{el} + P_1^{leak}$ is the applied heating power to stage 1. The calorimeter is operated in 2 modes (heating and cooling) where a constant power P_1 is applied and the temperature $T_1(t)$ is monitored. On heating a heating coil provides an accurately known heating power P_1^{el} while a control system keeps $|T_2\text{-}T_1| < 2\ 10^{-4}$ K, so that heat exhange $P_1^{leak} = K(T_2\text{-}T_1)$ (K is the thermal conductance) with the surrounding stage 2 at temperature T_2 can be neglected. In the cooling mode we use the heat leaks as a source of cooling power by maintaining $T_2\text{-}T_1$ at a constant negative value. The enthalpy change between a starting temperature $T_s(t_s)$ at a starting time t_s and $T(t)$ is

$$H(T) - H(T_s) = \int_{T_s}^{T_{tr}} C_p dT + \Delta H_L + \int_{T_{tr}}^{T} C_p dT$$

$$= P(t_i - t_s) + P(t_f - t_i) + P(t - t_f)$$

when continuously applying a constant power P. The term $P(t_f - t_i)$ is equal to the latent heat ΔH_L at the transition temperature T_{tr}. Thus the ASC method performs a direct measurement of the latent heat and of the enthalpy increase with changing temperature. Furthermore, typical ASC scanning rates are of the order of 1 mK/min so that thermodynamical equilibrium is approached. This is of great importance when phase transitions between equilibrium states are studied. Further details can be found in [5,6].

RESULTS AND DISCUSSION

High resolution ASC scans were performed at molar fractions of 0.0,

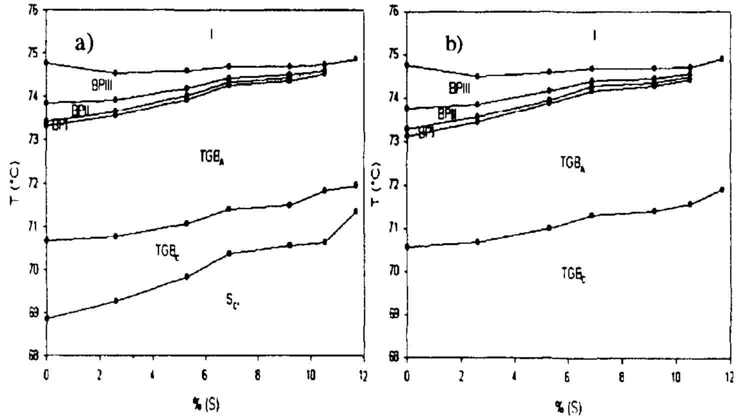

FIGURE 1 Phase diagram a) on heating and b) on cooling.

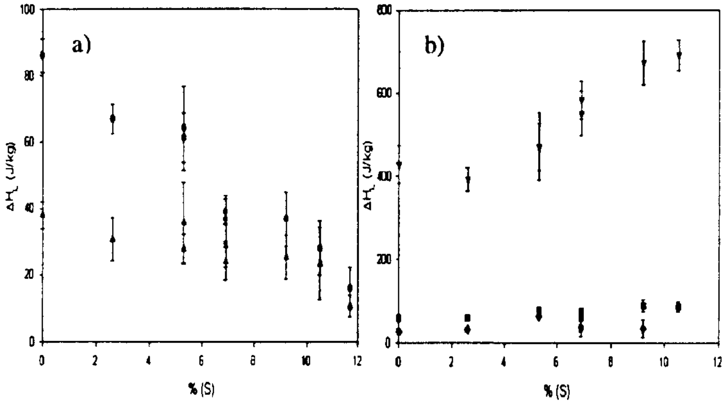

FIGURE 2 Latent heats as function of (S) fraction. a) S_{C^*}-TGB_C (▲), TGB_C-TGB_A (●) b) TGB_A-BPI (▼), BPI-BPII (◆), BPII-BPIII (■), presumed BPI-BPIII (▮).

2.6, 5.3, 6.9, 9.2, 10.5 and 11.7% (S) in the temperature range of 64 to 80°C. A phase diagram of the investigated region is shown in figure 1. The S_{C^*}-TGB_C transition is only observed on heating; this is explained by a supercooling of the TGB_C phase. Both this and the TGB_C-TGB_A transition are strongly first order. The width of the TGB_C phase clearly diminishes with increasing (S) concentration. This coincides with a clear descent of the TGB_C-TGB_A latent heat (see figure 2). Both indicate that the two TGB phases become more alike at lower chirality. It is expected that the TGB_C phase will dissapear at higher (S) fractions. A closer look at the S_{C^*}-TGB_C latent heats also reveals a descending

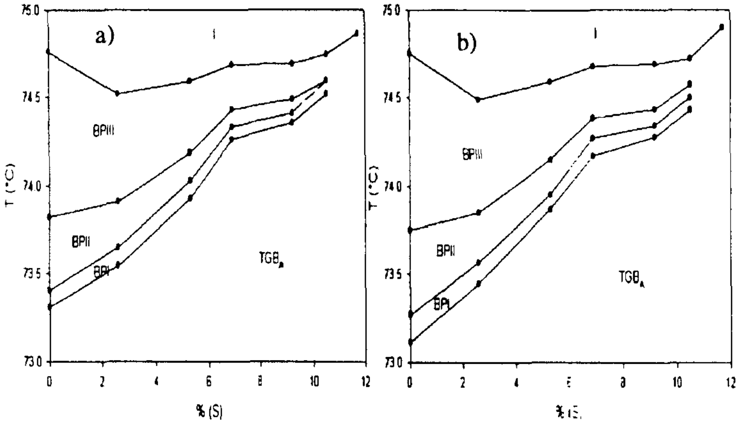

FIGURE 3 Detail of phase diagram in BP region a) on heating b) on cooling . Dashed line in a) : vanished BP at 10.5% is presumed BPII.

trend. From figure 3 one can see that the temperature region of the BPs diminishes at lower chirality. At a fraction of 10.5% (S) only two BPs are observed on heating, while all three are still present on cooling. The ASC method cannot determine the nature of the remaining phases. Due to the significantly larger temperature width of the BPIII region, it seems unlikely that this phase would dissapear. In similar cases [7,8] BPII vanishes first so we can assume the same for this system. However optical polarisation microscopic investigations at this precise composition could clarify this matter. At a fraction of 11.7% (S) all BP peaks have dissapeared, leaving a first order TGB$_A$-I transition with a latent heat of 3±0.3 kJ/kg. All TGB$_A$-BPI, BPI-BPII, BPII-BPIII as well as the presumed BPI-BPIII transition at 10.5% (S) are strongly

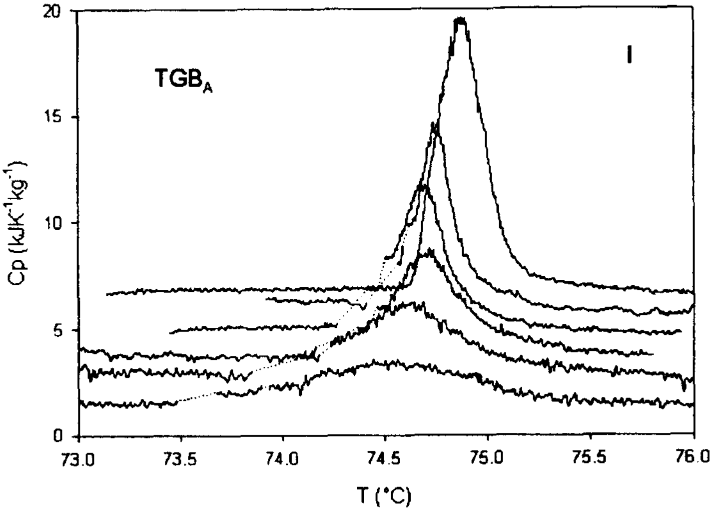

FIGURE 4 Evolution of C_p peak in the TGB$_A$-BP-I region for different (S) fractions. Dotted lines : superposed first order peaks are omitted for clarity. An offset of 1 kJK^{-1}kg^{-1} is added per fraction.

first order. The TGB$_A$-BPI latent heats are definitely increasing. The much smaller BPII-BPIII latent heats also show a slight increase, while the small BPI-BPII transitions do not show a clear evolution. From figure 4 it is obvious that for higher chirality (i.e. lower (S) fraction) the BPIII-to-isotropic $C_p(T)$ peak is not a real phase transition, but merely a supercritical C_p increase. However, the evolution towards a BPIII-I critical point, seems obvious. The BPIII-I enthalpy change at 10.5% indicates that the CP is very close to this composition. Apparently the most interesting behaviour is concentrated on the small composition interval between 10.5 - 11.7% (S). A further carefull ASC investigation of this region will elucidate whether this CP is experimentally accessible, i.e. whether the BPIII phase vanishes after it becomes first order. These scans together with precise optical investigations should reveal more details on the exact manner the BPs vanish in this region.

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