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HEXATIC AND CRYSTAL B PHASES IN A SERIES OF LIQUID CRYSTAL COMPOUNDS

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Abstract

Microscopy and miscibility techniques have been used to identify the hexatic B and crystal B phases of three pure compounds belonging to the same series. The physical behavior of smectic A, hexatic B and crystal B phases of these compounds has been studied by differential scanning calorimetry and dilatometry. Results on the smectic A to hexatic B and hexatic B to crystal B phase transitions are presented.

1) Introduction

Recently, several theoretical works have been reported on the melting of bidimensional systems. Kosterlitz and Thouless[1] have proposed a mechanism of melting of such systems. Halperin and Nelson[2] have shown that the smectic B phase with a tridimensional order must melt into a smectic A phase through another phase which has been called an hexatic B phase. The latter one has bidimensional layers without any correlation between them. In these layers, there is a long range orientational order, but a short range positional order. This theoretically predicted hexatic B phase has been found experimentally very recently.

Actually, there are only two known pure compounds which exhibit the hexatic B phase. The first one is the 4'-n pentyloxybiphenyl-4-carboxylate (65OBC), on which some physical studies[3,4,5] have already been performed.

The second one is the 4-propionyl-4'-n heptanoyloxyazobenzene. The occurrence of the hexatic B phase in this case has been demonstrated very recently by Goodby[6]. Moreover this compound exhibits both hexatic B and smectic

B tridimensional phases (we will note this phase crystal B in the following). In this letter we show that three other compounds belonging to the same series exhibit also the hexatic B phase. Then, we present some results on the behavior of the smectic A to hexatic B and hexatic B to crystal B phase transitions.

The compounds we have considered are the n=5,6,7 and 8 compounds of the series of the 4-propionyl -4'-n alkanoyloxyazobenzenes, the general chemical formula of which is the following :

$$H_5C_2-\underset{\substack{\|\\ O}}{C}-\emptyset-N=N-\emptyset-O-\underset{\substack{\|\\ O}}{C}-(CH_2)_n-CH_3$$

The n=5 term has been studied in detail by Goodby[6] who has found the existence of both hexatic B and crystal B phases. The other terms have already been synthesized by Poeti et al.[7]; they exhibit smectic A phases and other smectic phases, the identification of which has not been performed accurately.

2) Differential scanning calorimetry measurements

In their paper, Poeti et al. presented the DSC diagrams of the different terms of the series. The experiments reported there were performed with a Perkin Elmer DSC I type apparatus. We have redone these experiments with the much more sensitive Perkin Elmer type DSC II. In figure 1, we present the diagrams obtained for the four compounds of the series. These diagrams have been obtained by decreasing the temperature (2.5 degrees per minute) from the isotropic phase for each compound in the series.

We see immediately that the n=6 and n=7 compounds exhibit another phase transition, which has never been observed in these compounds; we observe a very small peak, which is similar to the one corresponding to the hexatic B → crystal B phase transiton of the n=5 compound. For the n=8 compound, no similar peak is detectable, whatever the rate of decreasing temperature and the sensitivity are.

Then we have performed miscibility experiments between the four compounds of the series. The miscibility diagrams are reported in figure 2. They correspond respectively to (n=5 and n=6), (n=6 and n=7), (n=7 and n=8) mixtures. These diagrams have been obtained by differential scanning calorimetry with a Perkin Elmer DSC II, in the same experimental conditions described above for the pure compounds. We have not been able to use the classical

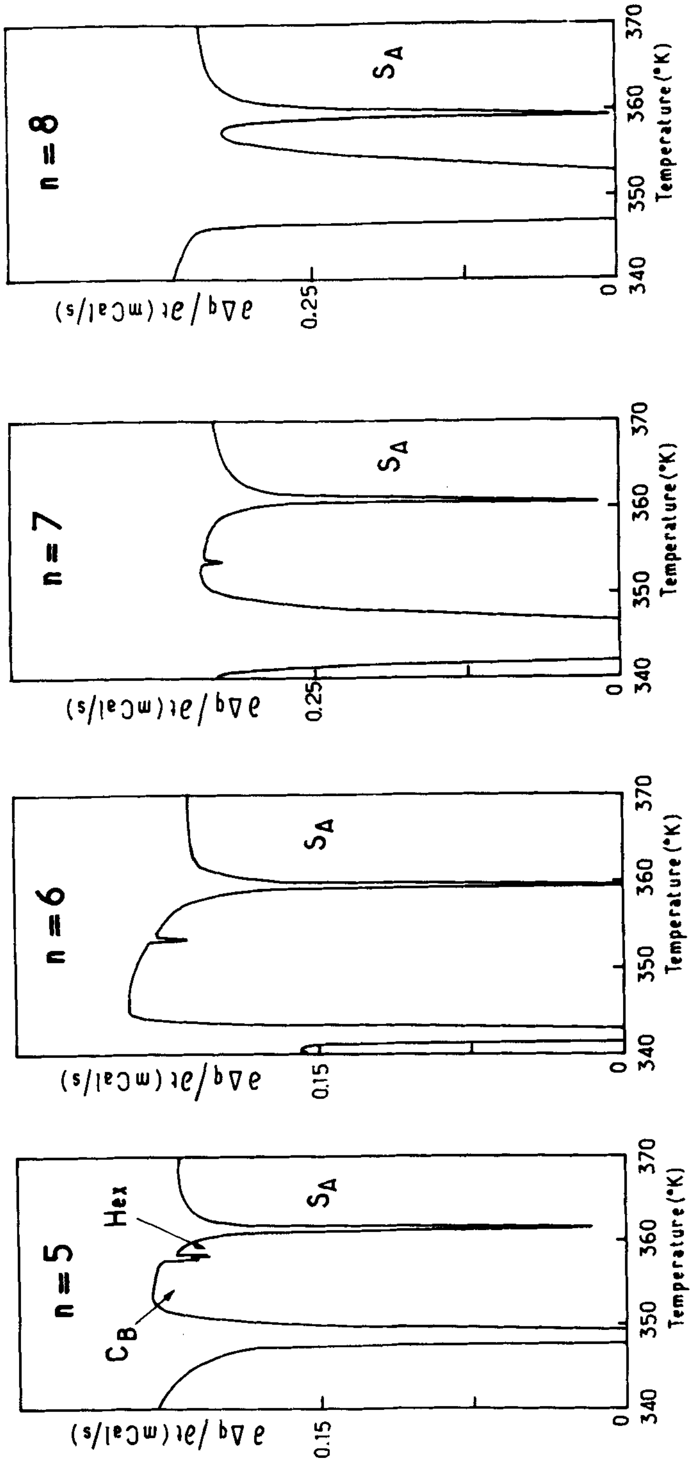

Figure 1 : DSC thermograms for the n=5,6,7 and 8 compounds

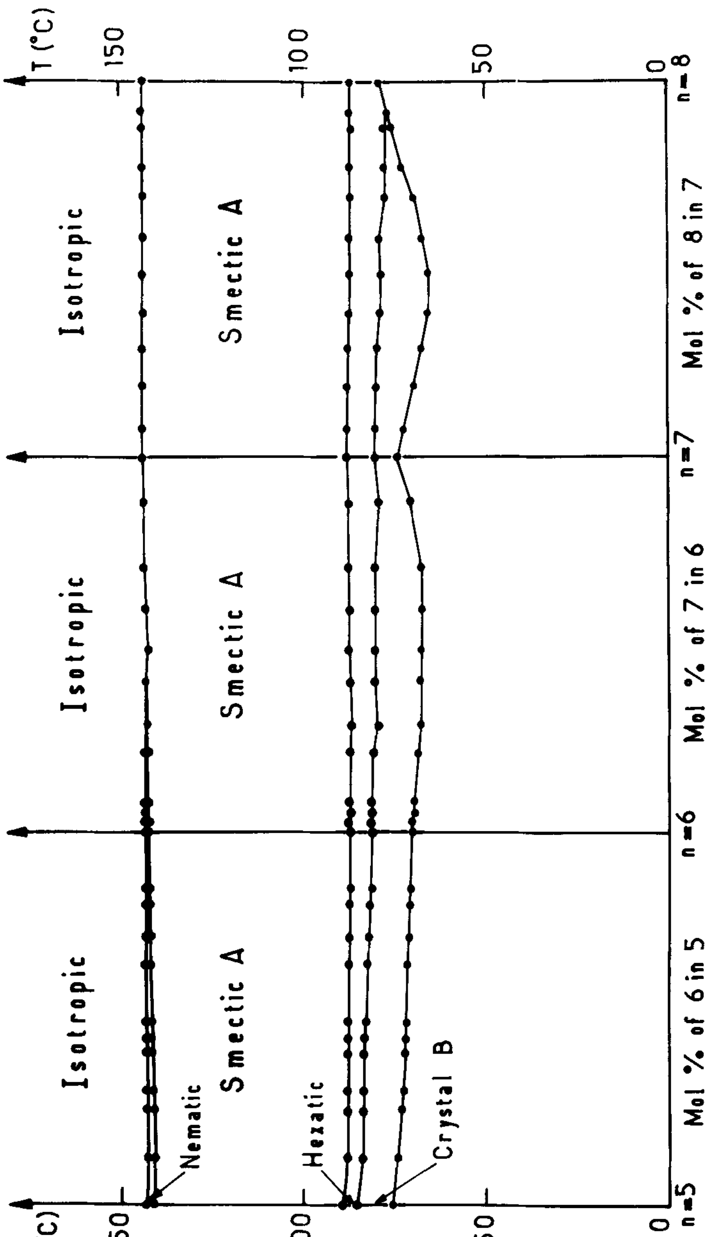

Figure 2 : Miscibility diagrams for the (n=5 and n=6), (n=6 and n=7) (n=7 and n=8) mixtures

miscibility method [8] with the polarizing microscope, due to the fact that the very small changes in the conic focal texture in the three phases are very difficult to detect.

From figure 2, we see that the n=6 and n=7 compounds exhibit hexatic B and crystal B phases, as the n=5 compounds does. The n=8 compound exhibits only a monotropic hexatic B phase.

The values of the transition temperatures and of the enthalpy variations corresponding to each compound are reported in Table I. The smectic A to hexatic B transition

Table I

n=5						
S_A	→	Hex	→	C_B	→	Crystal or ordered smectic
	88.7°C		85.4°C		75.8°C	
	1.04 Cal/g		0.05 Cal/g		6.46 Cal/g	
n=6						
S_A	→	Hex	→	C_B	→	Crystal or ordered smectic
	86.7°C		80.6°C		70.1°C	
	1.00 Cal/g		0.02 Cal/g		5.62 Cal/g	
n=7						
S_A	→	Hex	→	C_B	→	Crystal or ordered smectic
	87.9°C		80.1°C		74.3°C	
	0.99 Cal/g		0.02 Cal/g		13.76 Cal/g	
n=8						
S_A	→	Hex	→			Crystal or ordered smectic
	86.8°C		79.0°C			
	0.70 Cal/g		14.97 Cal/g			

is characterized by a transition enthalpy which is, significantly, quite large, (about 1 Cal/g). But the transition enthalpy for the hexatic B to crystal B transition is very small, of the order of 0.02 Cal/g for each compound in the series.

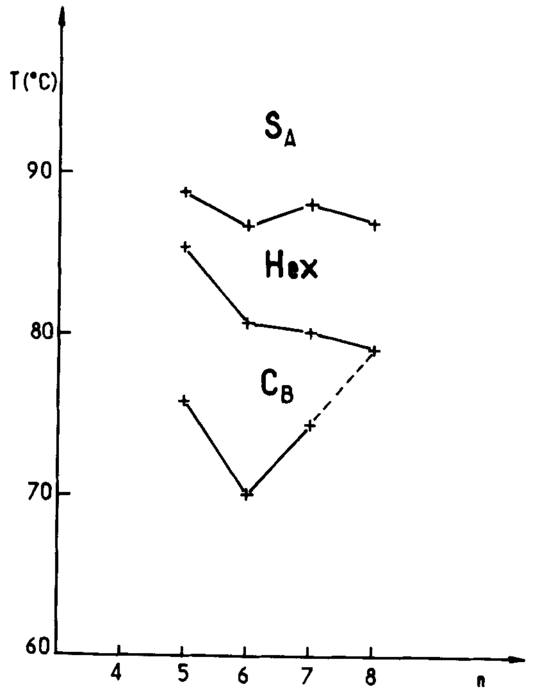

Figure 3 : Evolution of the transition temperatures as a function of the length of the aliphatic chain

Finally in figure 3, we have reported the values of the transition temperatures as a function of the length of the aliphatic chain . We see that the stability domain of the hexatic B phase is larger the longer the chain : indeed, for n=5, the hexatic B phase exists only within a 3°C range, whereas for n=8, it is detectable over about 9°C.

3) Observations in the optical microscope

The texture we observe in the polarizing microscope can be classical focal conic textures. The preparations can also appear uniformly homeotropic, especially for the n=5 and n=6 compounds. The focal conic textures in the smectic A phase remain identical when going into the hexatic B phase, then into the crystal B phase. We have not succeeded in detecting any change in the texture as a function of decreasing temperature within the stability domains of the three phases. This is in agreement with the observations already reported by Goodby and Pindak[3], especially for the smectic A to hexatic B phase transition.

For the n=5 and n=6 compounds we have obtained homeotropic textures very easily ; then conoscopic experiments show the uniaxiality of the smectic A phase, and also the uniaxiality of the hexatic B and crystal B phases. So, in the crystal B phase, we know the molecules are normal to the layers.

4) Dilatometric measurements

Using dilatometry, we have studied systematically the temperature dependence of the volume of each compound of the series. We report here only some partial results concerning the n=5 compound. The dilatometric measurements have been performed according to a method which has already been used for other liquid crystal compounds, and which has been described elsewhere [9].

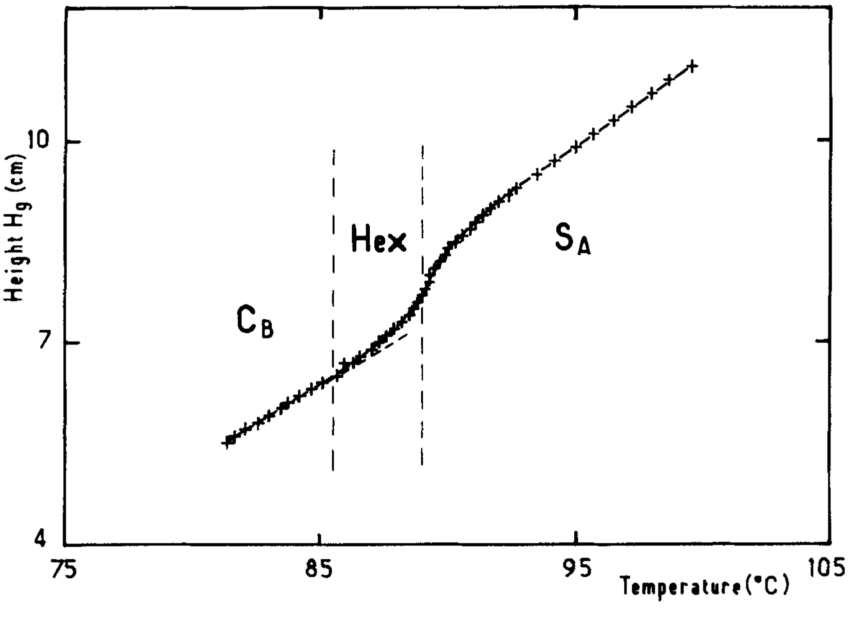

Figure 4 : Height of mercury as a function of temperature for the (n=5) compound

In figure 4, we show the variation of the mercury height (h) in the dilatometer capillary as a function of decreasing temperature in the three phases : smectic A, hexatic B and crystal B. We note an important variation of h at the smectic A to hexatic B transition, showing that this transition is first order, whereas Huang et al, by a specific heat study, have observed a second order behavior of the same transition in another compound.

The hexatic B to crystal B transition is much more difficult to detect ; at the time of our investigations we were only able to see a very slight change in the slope of the expansion coefficient of these two phases. A more detailed study of the volumetric variation as a function of temperature is in progress.

5) Conclusion

The different techniques used for the characterization of the liquid crystal compounds we have considered, have shown the existence of an hexatic B phase in three new compounds belonging to the same homologous series. Moreover, we have found the smectic A to hexatic B phase transition to be of first order (the corresponding jumps of volume and enthalpy are, significantly, large at this transition) ; on the contrary, the enthalpy and volume variations are very small at the hexatic B to crystal B transition. More detailed physical studies are in progress on these transitions in all the compounds of the series.

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