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CALORIMETRIC STUDY OF THE 4-PROPIONYL-4'-n-ALKANOYLOXY AZOBENZENE SERIES

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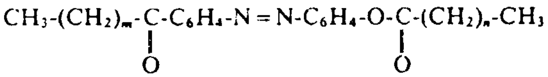
ABSTRACT: *Systematic DSC measurements have been performed on the different terms of the 4-propionyl-4'-n-alkanoyloxy azobenzene homologous series. Thermodynamical behavior as a function of the length of the aliphatic chain and recrystallization process are considered and discussed.*

INTRODUCTION

In two previous papers[1,2] one has reported the preparation and the transition temperatures of new series of mesomorphic compounds, the general chemical formula of which is:



$$\mathrm{CH_3\text{-}(CH_2)_m\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4\text{-}N=N\text{-}C_6H_4\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_n\text{-}CH_3}$$

with m = 0,1 and n ranging from 0 to 16.

Most of these compounds exhibit smectic A phases; the low members of the series (n = 8) exhibit in addition other smectic phases of different nature.

In this letter, we consider only the m = 1 series. First we report the transition energies of the different compounds and then discuss the nature of mesophases in some members of the series. In addition to the description of the thermodynamical behavior, we give evidence of the complex recrystallization of all the members of the series.

CALORIMETRIC MEASUREMENTS

They have been performed using a differential scanning calorimeter Perkin-Elmer DSC-2C calibrated with Indium metal samples. In general, the rate of increasing or decreasing the temperature was 2.5 °C/min.

In Figure 1a, we have represented the variation of the heat of transition between the solid phase and the smectic A phase as a function of

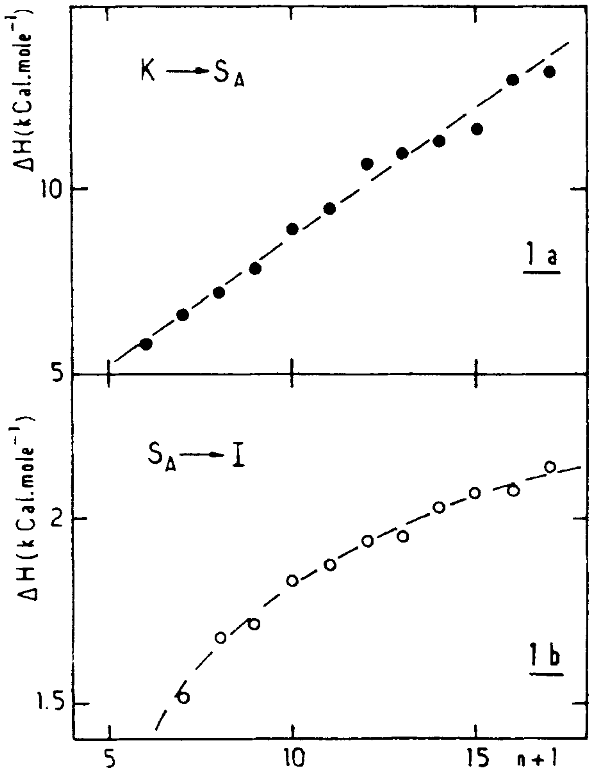


Figure 1: Heat of transition as a function of n.
a) solid (K) to smectic A (S_A) transition
b) smectic A (S_A) to isotropic (I) transition

the length of the aliphatic chain. It is clear that the heat of transition is linear function of n; therefore, from the slope of the line, we deduce a contribution of about 0.8 Kcal for each methylene group. This value is close to the value generally found for the same transition in other liquid crystalline series (0.9 Kcal/CH_2 group)[3]. It is related to the disorganization the aliphatic chains inducing the mesomorphic state.

In Figure 1b, we see that the heat of transition between the smectic A phase and the isotropic phase depends also on the length of the aliphatic chain. But in the case of that transition, the variation is no more linear. As far as n increases, the contribution of the aliphatic part of the molecules to the process of melting of the smectic A phase into the isotropic phase is less an less important.

n = 4 and n = 2 compounds

It has already been shown that four compounds of the series corresponding to n = 5,6,7 and 8 exhibit, monotropic hexatic and crystal B phases[4,5] in addition to the enantiotropic smectic A phase. In this letter, besides the smectic A phase, we discuss now the nature of the other smectic phases occuring in the n = 4 and n = 2 compounds.

For the n = 4 compound the first evidence of a monotropic smectic phase is given by looking at the DSC thermogram represented in Figure 2a. By cooling down from the smectic A phase, the thermogram exhibits two exothermic peaks located at 88°C and 82°C. One is reversible (see Figure 2b), whereas the other one is not reversible (see Figure 2c), indicating that the process of recrystallization has already occured.

We have performed miscibility experiments between the n = 4 term of the series and the hexiloxybenzylidene bromoaniline (6 Br) which is known to present a smectic B phase[6]. In Figure 3, is represented the miscibility diagram between the two compounds, where it is clear that the monotropic mesophase occuring in the n = 4 compound is of smectic B type.

In the case of the n = 2 compound, an enantiotropic mesophase is observed between 93°C and 120°C[2]. X-ray diffraction experiments show that this phase is an ordered smectic one. In the low angle region, there is an evidence of lamellar structure with at least four orders of diffraction, indicating a very well defined staking of the layers. The thickness of the layers is d = 20.7 Å and is independent of temperature. In the wide angle region, we observe a series of sharp reflexions, suggesting a pronounced order within the layers. When comparing with the layer spacing in the smectic A phase (d = 21.4 Å), we can conclude that this phase is a tilted smectic phase of H or G type[7], in agreement with the observation under the microscope showing textures with large mosaic domains in this phase.

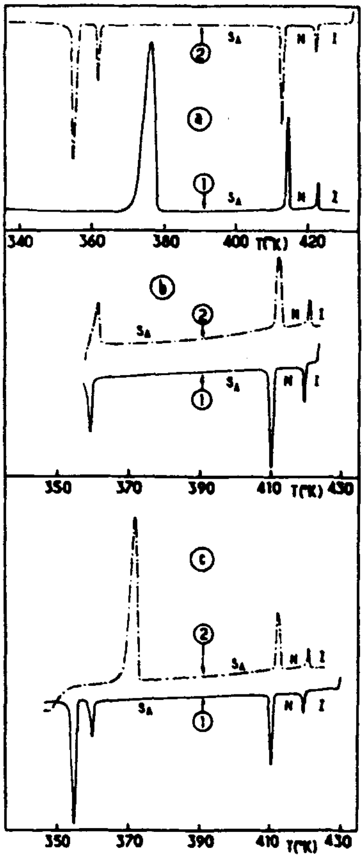


Figure 2: DSC thermograms for the n = 4 compound.
a) 1: heating run from the solid phase
2: cooling run from the isotropic phase
b) and c) 1: cooling run from the isotropic phase
2: heating run immediately after 1.

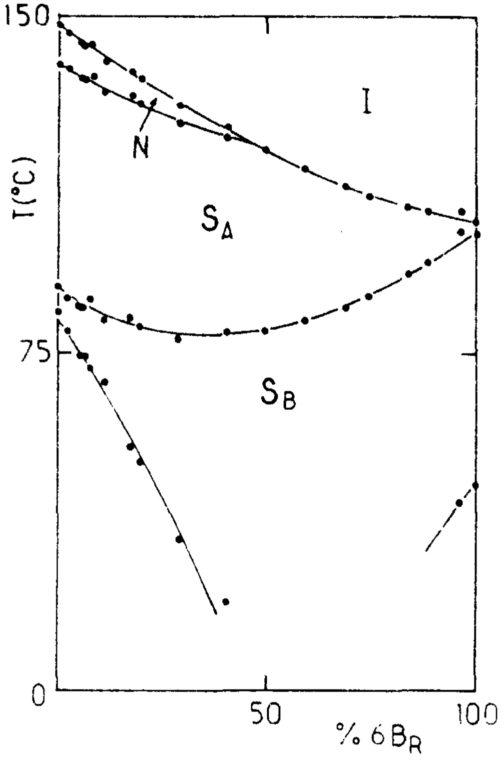


Figure 3: Miscibility diagram between the n = 4 and 6Br compounds

RECRYSTALLIZATION PROCESS

One interesting feature of all the compounds of the series is the way they come back to the solid phase. By cooling the temperature, DSC thermograms present, for each compound, one or several exothermic peaks occuring at various temperatures below the last smectic phase (see Figure 4); but anyways, in each case, on heating again the samples, we observe only the same endothermic peak corresponding to the transition between the solid and smectic A phases at a well defined temperature. This is an evidence of a very complex process for the compounds to pass from the mesomorphic state to the solid state, in the case of the series which is under consideration.

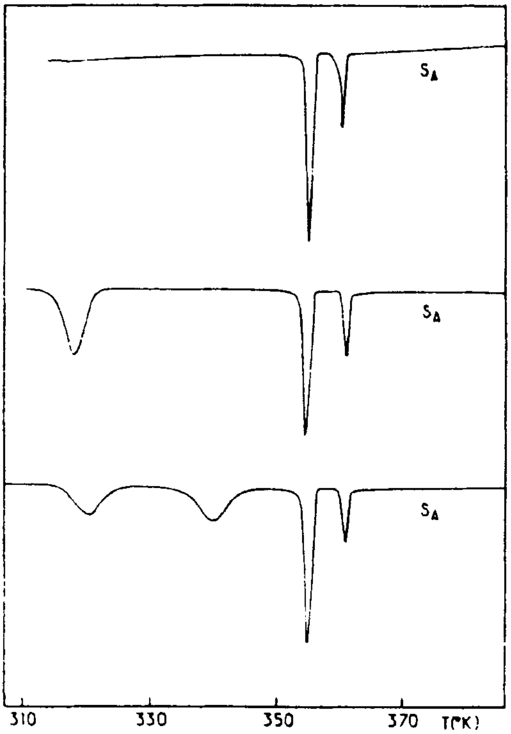


Figure 4: Different DSC thermograms of the n = 4 compound obtained by decreasing the temperature from the isotropic phase.

CONCLUSION

In Table I, we have summarized all our calorimetric investigation of the different terms of the series, associated with the determination of nature of the mesomorphic phases.

TABLE I: Temperatures of transition and enthalpies as function of n
(* = monotropic phase)

n	Transition		Temperature (°C)	Enthalpy (Kcal/mole)
2	K	$S_{H \text{ or } G}$	93	3.59
	$S_{H \text{ or } G}$	S_A	119.5	2.61
	S_A	N	136.5	0.98
	N	I	155.5	0.18
4	K	S_A	99	7.12
	S_A	N	138.5	0.94
	N	I	147.5	0.21
	S_A	S_B^*	88.5	0.65
5	K	S_A	92	5.93
	S_A	N	141.5	1.27
	N	I	143.5	0.22
	S_A	Hex*	88.7	0.38
	Hex*	S_B^*	85.4	0.02
6	K	S_A	96.5	6.57
	S_A	N	143	1.27
	N	I	143.5	0.24
	S_A	Hex*	86.7	0.34
	Hex*	S_B^*	80.6	0.01
7	K	S_A	94	7.21
	S_A	I	144	1.68
	S_A	Hex*	87.9	0.42
	Hex*	S_B^*	80.1	0.01
8	K	S_A	98	7.87
	S_A	I	144.5	1.72
	S_A	Hex*	86.8	0.26
9	K	S_A	97.5	8.96
	S_A	I	143.5	1.81
10	K	S_A	100.5	9.1
	S_A	I	143	1.88

TABLE I (continued)

11	K	S_A	101.5	10.7
	S_A	I	143.5	1.93
12	K	S_A	102.5	10.97
	S_A	I	140.5	1.94
13	K	S_A	103.5	12.31
	S_A	I	139	2.02
14	K	S_A	105.5	12.67
	S_A	I	137.5	2.06
15	K	S_A	106.5	14.04
	S_A	I	136.5	2.08
16	K	S_A	107.5	14.25
	S_A	I	135.5	2.14

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