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THERMODYNAMIC STUDY OF THE PHASE TRANSITIONS OF THE MESOGENS AND THE HOMOLOGOUS TRENDS OF THEIR MELTING ENTROPIES *

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ABSTRACT

The phase transitions of the nematogens EBAB and H*p*BAB were studied at various heating rates by the DSC method. Their thermodynamic data were obtained. It was revealed by the experiments that at room temperature the form of H*p*BAB K(g), which was obtained by repeated recrystallization from absolute ethanol, is a glassy crystal. On the basis of more reliable data, the linear relation of the melting entropy to the number of carbon atoms in the terminal alkyl group is presented for the homologous series. After improving Aranow's statistical approach, an analytical expression of the regression lines has been obtained, i.e.

$$\Delta S_m = \frac{\partial}{\partial T}[kT \ln(\psi_l/\psi_s)] + [R \ln(3/g)](n-1)$$

where $1 < g < 3$. From this, the homologous trends of the melting entropy have been interpreted.

INTRODUCTION

The most easily acquired (and sometimes the best) evidence for the relationship between molecular structures and properties of mesogens can be obtained with the aid of thermodynamic studies of their phase transitions. The *p*-*n*-alkyloxybenzylidene-*p*′-aminobenzonitriles are positively dielectric and thermotropic mesogens. Thermodynamic data of their phase transitions have been reported previously [1–6]. Moreover, Tsuji et al. [6] indicated correctly that the increment of the entropy of fusion in the homologues was ascribed only to the additional methylene group. However, there have been discrepancies among the thermodynamic data of the homologues, to various extents. The largest discrepancy occurs between the data of *p*-*n*-heptyloxybenzylidene-*p*′-aminobenzonitrile (H*p*BAB). The difference between its reported melting enthalpies is 43% or so [4,5]. In the case of its ethyl

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* Dedicated to Professor E.F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

homologue (EBAB), for which the number of carbon–carbon bonds in the alkyl group is the least, the discrepancy amongst the reported data [3,5] is also considerable. Therefore the phase transitions of H*p*BAB and EBAB are studied by DSC method in the present work. On the basis of the more reliable data, the homologous trends of the melting entropies are derived for this homologous series. By improving Aranow's [7,8] statistical approach, the nature of the above trends is expounded.

EXPERIMENTAL

Reagents

EBAB and H*p*BAB were purchased from the Shanhai Third Factory of Chemicals and the Beijing Institute of Chemicals, respectively. The latter was recrystallized repeatedly from absolute ethanol (AR grade) to constant melting point. Samples of both compounds were dried and kept in a desiccator before the DSC experiments.

Instrumentation

A Perkin-Elmer DSC-2C calorimeter was used in the present work. The determinations were performed using the automatic programs of a model 3500 Data Station. The temperature and power scales were optimally calibrated by use of high purity In, Sn, Pb and Zn.

PROCEDURE

Sealable aluminium pans were used in order to prevent vaporization, oxidization, hydrolysis, etc. The amount of sample employed was about 5 mg in order to reduce the space available to the gas phase as much as possible and to obtain a sufficiently large peak for the "clearing" process. Tinchurina et al. [9] declared that the dependence of the heat Q of the transition mesophase 1 $\rightleftharpoons$ mesophase 2 (or isotropic liquid phase) on the temperature scanning rates q is

$$Q = A + B \ln q$$

In a previous paper [10], the phenomenon of the increasing melting peak area for *p*-*n*-pentyloxybenzylidene-*p*′-aminophenyl butanoate with increasing q was observed, together with the participation of certain other structural changes, in the melting process. Kanetsuna et al. [11] reported the changing melting heats of polyethylene powder with changing heating rates in various types of DSC instruments. Kambe and Ozawa [12] ascribed this fact to other structural changes such as crystallization, etc. during the heating processes. Therefore it is necessary that all samples are determined at various rates—ranging from 1.25 to 10.00 K min^{-1} in the present work. The experiments show that the enthalpies of phase transitions of the samples under the investigation do not change with changing scanning rate. Consequently, it is inferred that there is no participation by the other structural changes in the phase transitions investigated. Furthermore, the additional heat resulting from the temperature gradient [9] is not included in the "clearing" enthalpies reported in this work.

RESULTS AND DISCUSSION

In the case of EBAB, the temperatures, enthalpies and entropies of the melting process (crystal K → nematic N) and the "clearing" process (N → isotropic liquid IL) were determined to be: 378.53 K, 26.48 ± 0.20 kJ mol^{-1}, 69.96 ± 0.53 J K^{-1} mol^{-1}; 399.80 K, 929 ± 53 J mol^{-1}, 2.32 ± 0.13 J K^{-1} mol^{-1}, respectively. These results are in agreement with those of Spratte and Schneider [3] within experimental error, except for those concerning the "clearing point" which is closer to that of Pisipati and Rao [13].

In the case of H*p*BAB, all samples were scanned between 260 and 381.5 K at various rates. Typical DSC curves are presented in Fig. 1. The solid samples K(g), obtained by recrystallization from absolute ethanol, were introduced into the calorimeter at 300 K and then cooled to 260 K. During the cooling, no heat capacity jumps and no detectable peaks were observed. The total peak area represented by ABCDE and the "clearing" peak area in Run 1, and the fusion peak area of the metastable crystal K(II) in Run 3 are in agreement with Smith's [4] melting enthalpy of stable crystal and its "clearing" enthalpy, and the melting enthalpy of metastable crystal, respec-

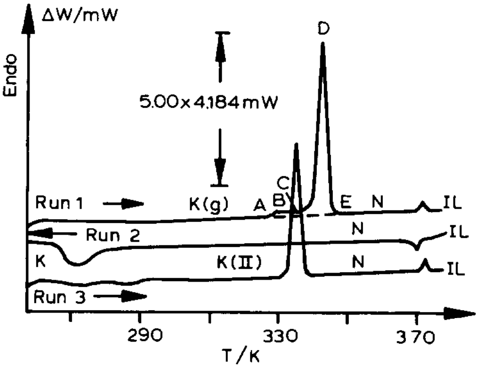

Fig. 1. Typical DSC curves (10 K min^{-1}): K, crystal; g, glassy crystal; II, crystal II; N, nematic; IL, isotropic liquid phase.

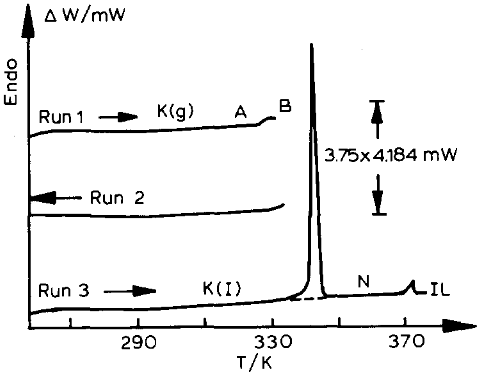

Fig. 2. DSC curves (10 K min^{-1}) revealing the glass transition and formation of the crystal K(I).

tively, within ± 1% or less. However, more detailed examination revealed that the segment AB and the subsequent plateau BC did not represent the melting process. The results are reproduced in Fig. 2. In Run 1 (Fig. 2) the sample K(g) was heated from 260 K and the heating was stopped at the point B just after the occurrence of the heat capacity jump (the highest temperature of B was 333.9 K in a series of measurements), and then, following Run 2, cooled to the starting temperature 260 K. No heat capacity jumps and no detectable peaks were observed in Run 2, indicating that the sample was still solid at point B in Run 1. The sample was heated again in Run 3 and a melting peak for the stable crystal K(I) and its "clearing" peak were obtained without the heat capacity jump observed in Run 1 (Fig. 1). In a separate experiment, a different sample K(g) was heated to point B, held isothermally for 1 h and then heated again at 5 K min^{-1}. A melting peak was obtained, its shape and area being the same as those represented by CDE in Fig. 1. Therefore it was concluded that the jump AB is not a part of the melting process, but is relevant to a glass transition. The crystal K(g), obtained by recrystallization from absolute ethanol, is a glassy crystal resembling the metastable crystal II of ethanol as observed by Haida et al. [14]. It is a crystalline material which undergoes the above glass transition on heating and then is melted directly, without undergoing an exothermic process of crystallization before melting. H*p*BAB is the first example of glassy crystal among the organic mesogens found so far, to the authors' knowledge. It is different from the glassy liquid crystal. The latter is changed into a mesophase (nematic, cholesteric or smectic) after its glass transition during heating. It was found that the melting peak area of K(I) was 4% larger than that of K(g) as calculated from the peak CDE in Fig. 1. The onset temperatures of K(I) and K(g), which are taken as their melting points, differ by only a few tenths of a degree. Considering the above and by inspecting Fig. 2, it can be concluded that the glassy crystal K(g) is a non-equilibrium state of the stable crystal K(I). The melting point and

TABLE 1

DSC determination of temperature and enthalpy of phase transition of H*p*BAB

No.	Heating rate (K min^{-1})	Glass transition		K′ (g) [a] → N		N → IL		K(II) → N	
		T_g (K)	ΔC_p(J K^{-1} g^{-1})	T_m (K)	ΔH_m (J g^{-1})	T_c (K)	ΔH_c (J g^{-1})	T'_m (K)	$\Delta H'_m$ (J g^{-1})
A	10.00	327.28	1.09	340.77	96.69	370.57	2.18	332.92	70.75
B	10.00	327.11	0.962	340.60	97.36	370.58	2.30	332.67	70.96
C	10.00	327.60	1.13	340.90	98.11	370.92	2.18	332.70	71.09
D	10.00	326.85	0.837	340.71	98.49	370.51	2.22	[b]	[b]
H	10.00	326.40	0.879	340.74	98.03	370.56	2.26	332.31	71.73
E	5.00	327.00	0.879	340.71	98.32	370.66	2.26	332.35	70.71
F	5.00	326.94	1.00	340.88	98.20	371.09	2.22	332.26	70.25
G	2.50	Too small		340.74	98.45	370.92	2.22	331.94	70.25
Mean ± 2σ		327.05 ± 0.41	0.968 ± 0.085	340.74 ± 0.10	97.96 ± 0.44	370.63 ± 0.15	2.23 ± 0.03	332.65 ± 0.25	70.73 ± 0.28

[a] Crystal form that underwent the glass transition in sample of original glassy crystal.

[b] Melting peak of K(I).

All transition temperatures calculated from extrapolated onset points in this work.

Mean values of transition temperatures obtained by averaging over the values determined at 10 K min^{-1} which is the same as the rate used in calibration.

σ is the standard deviation of the mean value.

TABLE 2

DSC determination of temperature and enthalpy of phase transition of stable crystal K(I)

No.	Heating rate ($K\ min^{-1}$)	K(I) → N		N → IL	
		T_m (K)	ΔH_m ($J\ g^{-1}$)	T_c (K)	ΔH_c ($J\ g^{-1}$)
D	10.00	341.25	102.5	371.41	2.26
L	10.00	341.22	102.8	370.96	2.22
M	10.00	341.02	102.6	370.83	2.26
N	1.25	340.77	101.3	ND	ND
Mean $\pm 2\sigma$		341.16 ± 0.14	102.3 ± 0.7	371.07 ± 0.35	2.25 ± 0.03

For samples L, M and N, data are from the scanning results on reheating, after stopping the scanning at point B and then depressing temperature to 260K.
ND, not detected.

enthalpy of the metastable crystal K(II) are considerably lower than those of K(I). Even after long annealing at 323.7 K it was not changed into K(I). The thermodynamic data of glass transition, fusion of K(g), K(I) and K(II), and their "clearing" processes are summarized in Tables 1 and 2. It can be seen that the results of enthalpy determinations are not influenced by the change in scanning rate. For the stable crystal K(I), $T_m = 341.16 \pm 0.14$ K, $\Delta H_m = 32.78 \pm 0.22$ kJ mol^{-1}, $\Delta S_m = 96.07 \pm 0.66$ J K^{-1} mol^{-1}; for the metastable crystal K(II), $T_m' = 332.65 \pm 0.25$ K, $\Delta H_m' = 22.66 \pm 0.09$ kJ mol^{-1}; for the nematic phase from the melting of K(I), $T_c = 371.07 \pm 0.35$ K, $\Delta H_c = 721 \pm 9$ J mol^{-1}, $\Delta S_c = 1.94 \pm 0.03$ J K^{-1} mol^{-1}; for the glass transition of K(g), $T_g = 327.05 \pm 0.14$ K, $\Delta C_p = 310 \pm 27$ J K^{-1} mol^{-1}. Smith's [4] value of the melting enthalpy of stable crystal agrees with that obtained from the peak area of ABCDE in Fig. 1 to within about 1%. According to the statement that the segment AB does not represent part of the melting process, Smith's melting enthalpy of the stable crystal may be slightly higher and could include the abnormal part of the heat capacity.

For the homologous series *p*-*n*-alkyloxybenzylidene-*p*′-aminobenzonitriles, the thermodynamic data of EBAB and H*p*BAB have been determined as mentioned above. For the homologues in which the carbon number of the alkyl group (*n*) is 4, 6 or 8, Smith's [4] melting enthalpies can be verified very well by different methods. Furthermore, the melting entropy can be calculated by use of the relation

$$\Delta S_m = \Delta H_m / T_m$$

Incorporating Billard et al's [2] data for the $n = 10$ homologue, the homologous trend of the melting entropy $\Delta S_m(K \rightarrow N)$ versus the carbon number of the alkyl group have been derived and are shown in Fig. 3. It can be seen that there are two linear regression lines (correlation coefficients: 0.97 and 0.94). This suggests that the melting entropies of the various homologues can be represented by a linear function of the number $(n-1)$ of carbon–carbon bonds in the alkyl groups. Both the lines have nearly the same intercepts but different slopes. There is an jump of 17.4 J K^{-1} mol^{-1} at $n=7$. Tsuji et al. [6] reported also a similar tendency for this homologous series in their study of the $n=6$ homologue. In the present work, the homologous trends are investigated on the basis of a statistical model.

In the homologous series investigated, each member differs only in the number n of carbon atoms of the alkyl group, the aromatic part of the molecules being completely the same. It would be expected that the aromatic part should have the same degree of freedom of molecular motion under similar conditions for each molecule in this series. Consequently, the homologous trend of the melting entropy in this series should resemble that for the corresponding n-alkanes. For the n-alkanes and their derivatives, Aranow [7,8] has presented a statistical model, the so-called model of pseudo-degenerate torsional oscillators, for the restricted rotations of CH_2 groups around their carbon–carbon bonds. On the basis of experiment and the above theory, Aranow [7,8] indicated that the entropy of fusion of n-alkanes increases by an increment of $R \ln 3$ (i.e. 9.13 J K^{-1} mol^{-1}) for each additional CH_2 group added to the chain, especially for $n < 20$. In the case of Schiff's bases, this increment for each additional CH_2 group is far less than $R \ln 3$. This difference could be due to the presence of the aromatic part in these molecules. The latter influences the thermal motion of the alkyl group by either intramolecular or intermolecular interactions. For the case where the long chain molecules are surrounded by the molecules of mixed solvents (water and an organic solvent which is soluble in water to a large extent), Aranow [8] introduced the g factor into the partition function of the β phase, and derived the result $3/g$ $(1 < g < 3)$ for the equilibrium distributions between α and β phases. He explained the deviation from the "rule of three". Therefore in the case of melting entropy of the Schiff's bases, the partition functions

$$Z_s = \psi_s \left[\sum_j g \exp(-\epsilon_j/kT) \right]^{(n-1)N}$$

and

$$Z_l = \psi_l \left[\sum_i 3 \exp(-\langle \epsilon_i \rangle/kT) \right]^{(n-1)N}$$

are obtained for the solid(s) and liquid-melt (l) phases, respectively, by introducing the g factor into the partition function of the solid phase. From Aranow's [8] equation (10) of melting entropy

$$\Delta S_m = -\frac{\partial}{\partial T}[-kT \ln(Z_l/Z_s)]$$

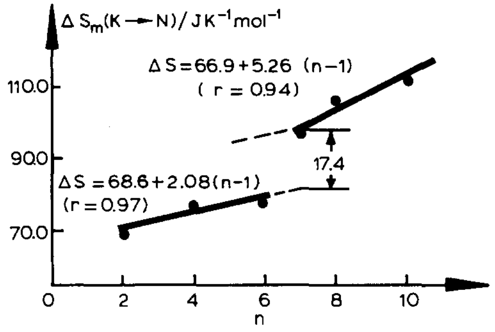

Fig. 3. Relation of the melting entropies $S_m(K \rightarrow N)$ to the numbers of carbon atoms n. ●, Experimental value; ———, the best fitting line by means of linear regression; — — —, extrapolated line with suitable slope; for $n = 10$, $S_m(K \rightarrow N) = S_m(K \rightarrow S_a) + S(S_A \rightarrow N)$, where S_A is smectic phase A.

a modified form of Aranow's equation (11) is acquired as follows

$$\Delta S_m = \frac{\partial}{\partial T}(kT \ln \psi_l/\psi_s) + (Nk \ln 3/g)(n-1)$$
$$+ \frac{\partial}{\partial T}\left\{(n-1)NkT \ln\left[\sum_i \exp(-\langle\epsilon_i\rangle/kT)/\sum_j \exp(-\epsilon_j/kT)\right]\right\}$$

which contains the g factor in this work. Following Aranow's arguments [7,8], the first term on the right-hand side of the above equation is a constant and the third term is negligible. Consequently, for 1 mole of material the melting entropy is approximately

$$\Delta S_m = \frac{\partial}{\partial T}[kT \ln(\psi_l/\psi_s)] + (n-1)R \ln(3/g) \quad (1 < g < 3)$$

This equation is in agreement with analytical expressions of the linear regression lines in Fig. 3. The intercepts of both the best fitting lines are nearly the same, within about 1% for the enthalpy determinations. According to Aranow [8], matching intercepts imply that the terms related to the ratio ψ_l/ψ_s are approximately constant for both $n \leqslant 6$ and $n \geqslant 7$. That is to say, all the contributions other than the torsional oscillation of CH_2 groups are also approximately the same in both cases. The presence of the aromatic part of the molecules results in the slopes of both the fitting lines being far less than the slope of n-alkanes, $R \ln 3$. This is a deviation from the "rule of three" in the case of the melting entropy. Because the size of the aromatic part is constant, it would be expected that the g factor would approach unity when the length of alkyl chain is very long. Consequently, the slope is larger and the g factor is less when $n \geqslant 7$ than when $n \leqslant 6$.

The entropy jump, which is 17.4 J K^{-1} mol^{-1} in Fig. 3, is far more than $R \ln 3$. Unfortunately, the data of the entropies of crystal–crystal transition are very scarce in the literature for this homologous series. However, our observations for the $n = 2$ and 7 homologues, and our preliminary observation for the $n = 4$ homologue show the absence of a crystal–crystal transition before the melting transitions of their stable crystals. Moreover, Smith's [4] melting enthalpy is well in agreement with Levine and Tomeczek's [5] datum and our preliminary observation for the $n = 4$ homologue. But Tsuji et al. [6] showed that there was a crystal–crystal transition not very long before the melting transition of crystal I of the $n = 6$ homologue and that the entropy of the crystal–crystal transition was 16.7 J K^{-1} mol^{-1}. The latter value is very close to this entropy jump (17.4 J K^{-1} mol^{-1}). Furthermore, the sum of Smith's melting entropy and Tsuji's entropy of the crystal–crystal transition for the $n = 6$ homologue is also in agreement with the upper dashed line in Fig. 3 at $n = 6$. But according to the statistical equation of melting entropy in this work, the entropy jump results from the slope variation just at $n = 7$. Briefly, the homologous trends of the melting entropies are to be ascribed to the torsional oscillation of CH_2 groups and the influence of the aromatic part on the thermal motion of the alkyl chains, which results in the slope variation.

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