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Calorimetric Study on Optically Isotropic Liquid Crystals*

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Heat capacities of optically isotropic mesogens, BABH(8), ANBC(16) and ANBC(18), have been measured by adiabatic calorimetry. The existence of solid-solid phase transitions with large entropy change seems to play a characteristic role for formation of the isotropic mesophase. Entropies of transition between the isotropic mesophases and the neighboring liquid crystalline phases are quite small. On the basis of the entropies of transition the possibility is suggested that the molecules might be aggregated in an identical manner in these two phases.

Keywords: isotropic mesophase; thermotropic mesophase; heat capacity calorimetry; entropy of transition; cubic mesogen

INTRODUCTION

Thermotropic liquid crystals are usually characterized as optically anisotropic liquids. In contrast, optically isotropic mesophases have been known in lyotropic systems, where spherical or rod-micelles consisting of amphiphilic molecules form higher-order cubic structure and solvent molecules fulfill the large interstices in the "lattice".

Quite interestingly, there have been reported rare examples of optically isotropic phases even in thermotropic liquid crystals, 4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acid {ANBC(*n*_C), *n*_C: the number of carbon atoms in an alkoxy chain, *n*_C = 16, 18}^[1] and 1,2-bis(4-*n*-alkoxybenzoyl)-hydrazine {BABH(*n*_C), *n*_C = 8, 9, 10}^[2] (Fig. 1). Demus et al.^[3] designated the cubic mesophases of ANBC's as smectic D in 1968, and on the basis of X-ray diffraction Diele et al.^[4] speculated a body-centered-cubic structure model

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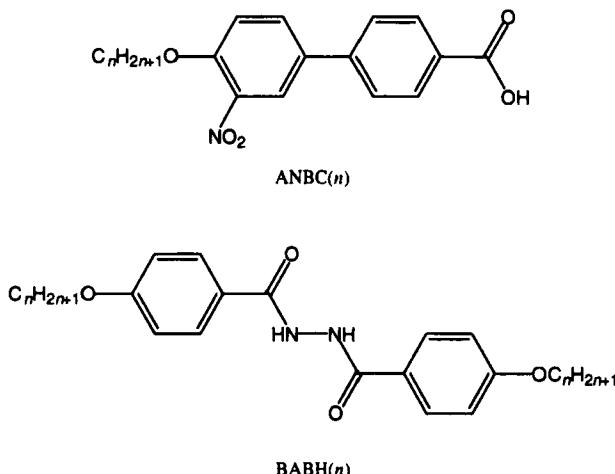


FIGURE 1. Molecular structures of ANBC and BABH.

consisting of spherical micelles in 1972. From the analogy of lyotropic systems, Tardieu and Billard^[5] proposed an interwoven, three-dimensional jointed-rod micelles structures with overall cubic symmetry. Since the cubic symmetry is incompatible with the smectic layered structure, the mesophase is now called simply the D or CubD phase^[6]. Since the CubD phases of ANBC's appear at high temperature side of smectic C (SmC) while the cubic phases of BABH's locate at low temperature side of SmC, Demus *et al.*^[2] regarded these two cubic mesophases as having different structures.

Nowadays a longstanding debate concerning the structure of the D phase of ANBC seems to converge to the model by Tarreau and Billard^[5]. It is then of great interest to examine whether the cubic phase of BABH is different from the CubD phase of ANBC. Besides, it is evident that the establishment of the structural model is not the goal but a starting point of the statistical modeling of the isotropic mesophase at the molecular level. Detailed thermodynamic study is crucial in such a context, because any molecular models of phase transition are assessed through the comparison with thermodynamic data, and especially because the unit cell of the isotropic mesophase contains more than hundreds molecules, the number of which fluctuates both in space and time. This situation prompted the authors to start the thermodynamic study of the isotropic mesogens^[7-10].

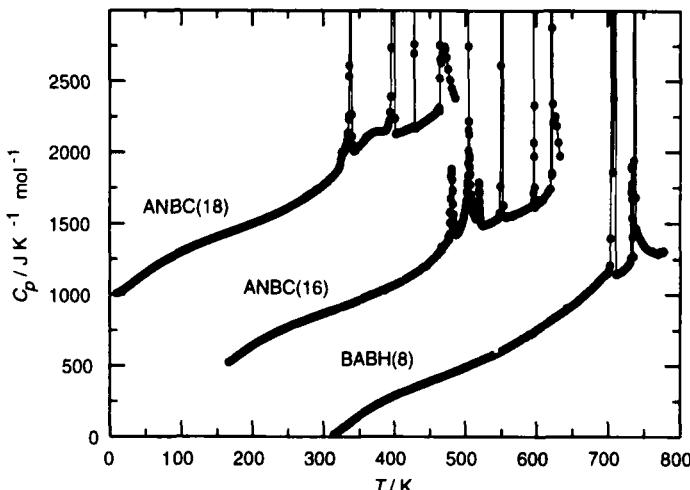


FIGURE 2. Molar heat capacities of BABH(8), ANBC(16) and ANBC(18). The scale for the abscissa is for ANBC(18), and other plots are shifted by a step of 150 K. The scale for the ordinate is for BABH(8), and other plots are shifted by a step of 500 J K⁻¹ mol⁻¹.

EXPERIMENTAL

BABH(8) was synthesized by condensation reaction between *p*-*n*-octyloxybenzoyl chloride and hydrazine in non-aqueous solvent (pyridine), and purified by repeated recrystallization from ethanol^[8]. ANBC(*n*_C) (*n*_C = 8, 16, 18) were synthesized starting from 4'-hydroxybiphenyl carboxylic acid, 1-bromoalkanes and fuming nitric acid, and purified by repeated recrystallization from ethanol. The quality of the specimen was checked by elemental analysis, ¹H-NMR, and mass-spectrometry, which showed no impurities.

Heat capacities of the isotropic mesogens BABH(8), ANBC(16) and ANBC(18) were measured by using adiabatic calorimeters^[11,12]. About 3 g of the polycrystalline sample was sealed in a calorimeter vessel with helium gas for heat exchange. The experimental details and numerical data have separately been given for each sample elsewhere^[8-10].

RESULTS AND DISCUSSION

Figure 2 shows the heat capacities of BABH(8)^[8], ANBC(16)^[9] and ANBC(18)^[10]. Their melting points were determined as 410.58 K, 401.12 K and 399.42 K, respectively. Using the data of melting points and enthalpies of

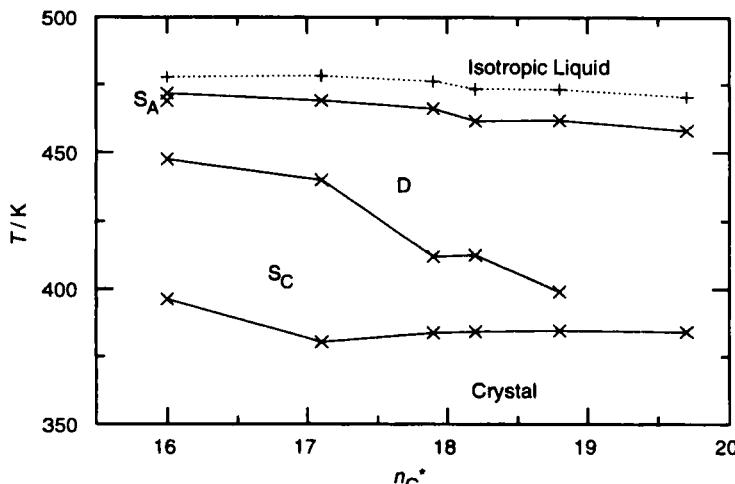


FIGURE 3. Transition temperatures in ANBC(16) - *n*-tetradecane system plotted against n_C^* .

fusion, the purity of the samples used for calorimetry was determined by means of the fractional melting method, which utilizes the proportionality between the content of impurity and the melting point depression. The results showed the purities of the samples are better than 99.5 mole per cent.

In all the compounds, there exist solid-solid phase transitions with a fairly large enthalpy/entropy gain^[8-10]. This is in strong contrast to the trend that large solid-solid phase transitions are rarely observed in classical rod-like mesogens, i.e., nematogen and smectogen^[13]. On the contrary, such transitions are known to be a necessary condition for appearance of columnar mesophases, where the alkyl chains attached to the central moiety are in nearly complete disorder in terms of entropy^[14]. It is known that the contributions to entropy by *gauche-trans*-type reorientational disorder of a methylene and a methyl group are 10.31 J K⁻¹ mol⁻¹ and 3.78 J K⁻¹ mol⁻¹, respectively^[14]. The accumulated excess entropy due to phase transitions is 119.26 J K⁻¹ mol⁻¹ for BABH(8) by the cubic phase. This is smaller than the value expected for complete conformational disorder of the alkoxy chains (152 J K⁻¹ mol⁻¹). Similarly, the expected and observed entropies are 158 J K⁻¹ mol⁻¹ and 148.46 J K⁻¹ mol⁻¹ for the CubD phase of ANBC(16), and 179 J K⁻¹ mol⁻¹ and 151.52 J K⁻¹ mol⁻¹ for the CubD phase of ANBC(18). Although the observed values of the excess entropy are smaller than the expected ones, they are comparable, implying the alkoxy chains are in, not completely but highly, disordered state in the isotropic mesophases.

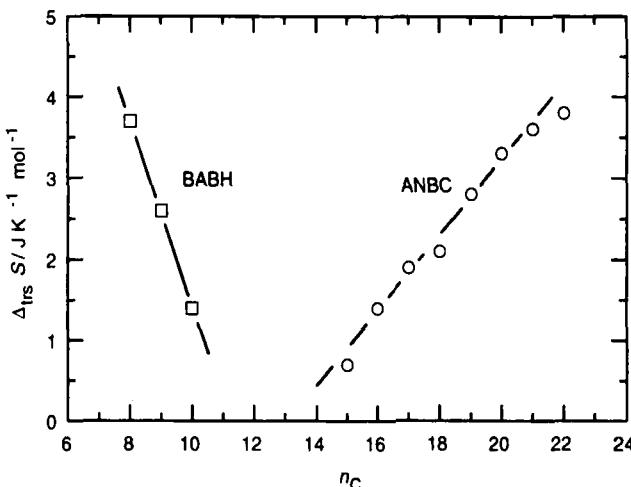


FIGURE 4. Entropy of transition between the isotropic mesophase and the SmC phase as a function of the alkoxy chain length.

Highly disordered state of the alkoxy chains suggests that the alkoxy chains in the isotropic mesophases play a role of solvent in lyotropic systems. To see the validity of this hypothesis, the phase behavior of the binary system ANBC – *n*-tetradecane was examined using DSC[7]. The resulting phase diagrams are conveniently compared in terms of n_C^* , the number of paraffinic carbon atoms per ANBC core. The n_C^* dependence of transition temperature for the system ANBC(16) – *n*-tetradecane is shown in Fig. 3. The n_C^* dependence in the ANBC(16) or ANBC(18) – *n*-tetradecane system is apparently similar to the n_C dependence of the neat series of ANBC's[15]. This fact clearly demonstrates that the terminal alkoxy chains in the D phase behave, at least in part, like a solvent. More precisely, the volume fraction of paraffinic carbon atoms (and hydrogen atoms attached) governs the temperatures of the SmC – CubD and the CubD – isotropic liquid phase transitions. The CubD phase is not induced in the ANBC(8) – *n*-tetradecane system.

In contrast to the large solid-solid phase transitions, the phase transitions between the isotropic mesophase and other liquid crystalline phases are quite small in spite of their large difference in the higher-order structures[8-10]. For example, the enthalpy and entropy of the cubic – SmC transition is 0.98 kJ mol⁻¹ and 2.26 J K⁻¹ mol⁻¹, respectively for BABH(8). The energetic similarity between the isotropic mesophase and the layered structure of SmC phase favors the interwoven jointed-rod structure rather than the spherical micelle structure of the isotropic mesophase because the latter costs the curvature elastic energy (splay energy) in contrast to possible cancellation around the saddle point in the former.

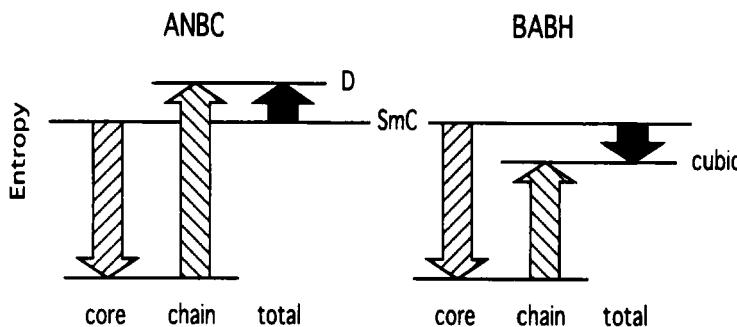


FIGURE 5. "Alkyl-chains as Entropy-reservoir" mechanism for the inverted phase sequence in ANBC (SmC \rightarrow CubD on heating) and BABH (cubic \rightarrow SmC).

It is surprising that the entropy of SmC – CubD transition in ANBC(18) ($2.66 \text{ J K}^{-1} \text{ mol}^{-1}$)^[10] is much larger (by a factor of 1.6) than that of ANBC(16) ($1.63 \text{ J K}^{-1} \text{ mol}^{-1}$)^[9], because the molecular size differs only slightly. Such a strong dependence of entropy of transition have been reported on the basis of DSC experiment for ANBC's^[15] and BABH's^[2]. The entropies of transition between the SmC phase and the isotropic mesophase are plotted against n_C in Fig. 4. Linear relations with opposing signs of the slope are recognized for ANBC's and BABH's. This plot clearly shows that the conformational degrees of freedom of the alkoxy chain are relevant to these transitions. Taking into account the inverted phase sequences between ANBC's and BABH's it is also evident that the alkoxy chain is in a more disordered state in *both* isotropic mesophases than the SmC phase^[10]. The seemingly large slope of BABH's is reasonable because BABH(n_C) has a "doubled" molecular structure in an isolated state. It is noted that ANBC(n_C) molecules are dimerized via hydrogen bonds^[16]. The contribution of a methylene group to the entropy gain is, thus, estimated as about $0.5 \text{ J K}^{-1} \text{ mol}^{-1}$ from the slopes for BABH and ANBC. On the other hand, there is a very curious question why a long alkoxy chain does not contribute directly to the entropy of transition. One may, hence, imagine that an alternate negative contribution should exist, which might be attributable to the rest of the molecule, i.e., the "dimerized core".

The same contribution from a methylene group clearly demonstrates that the two isotropic mesophases are very similar in terms of disorder of terminal alkoxy chains, implying the identity of the two phases. Assuming the identity, the upper and lower bounds for the entropy change due to the "dimerized core" are estimated from Fig. 4 to be $13 \text{ J K}^{-1} \text{ mol}^{-1}$ and $6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, upon the transition from the isotropic mesophase to the SmC phase^[10].

The contribution of the core and the alkoxy chain to the entropy of transition thus estimated have opposing signs. Since a phase with larger entropy is more stable at high temperature, the "core" arrangement prefers the

SmC phase at higher temperature whereas the chain the isotropic phase. This competition accounts for the inverted phase sequence in ANBC (SmC \rightarrow CubD on heating) and BABH (cubic \rightarrow SmC) as shown in Fig. 5. This mechanism may be described as "Alkyl-chains as Entropy reservoir". The failure of the miscibility between these two cubic phases^[2] may originate in this inverted phase sequence, which is caused by the difference in the chain length or the molecular size.

The phase transitions^[14,17] and glass transitions^[18,19] in which the intramolecular degree(s) of freedom plays a primary role have been identified so far. Since the conformational disordering of alkoxy chains only modifies the phase sequence in the "Alkyl-chains as Entropy reservoir" mechanism, this mechanism is of new type of the influence that the intramolecular degrees of freedom bring on macroscopic phase behavior.

CONCLUSION

From thermodynamic study on the cubic mesogens BABH(8), ANBC(16) and ANBC(18) and related systems, the following conclusions are derived.

1. The cubic mesogens commonly exhibit large solid-solid phase transitions^[8-10]. These phase transitions are related to the disordering process of the terminal alkoxy chains. The terminal chains are not completely but highly disordered in the isotropic mesophases.
2. This highly disordered alkoxy chains in the isotropic mesophase behave, in part, like a solvent in lyotropic systems^[7].
3. Small enthalpy of transition between the isotropic mesophases and the neighboring liquid crystalline phases is favorable to the interwoven jointed-rod model of the higher-order structure for the cubic mesophases^[8].
4. The terminal alkoxy chains are in more disordered state in the isotropic mesophases than in the SmC phase whereas the spatial arrangement of the molecular core is more ordered in the cubic phase than in the SmC phase^[10].
5. The magnitude of the contribution from a methylene group to the entropy of transition from the isotropic mesophase to the SmC phase is identical in ANBC's and BABH's. This strongly suggests that the CubD phase of ANBC and the cubic phase of BABH are identical in nature^[10].
6. The opposite sign of the contributions of the terminal chain and the molecular core can explain the inversion of the phase sequence between ANBC (SmC \rightarrow CubD on heating) and BABH (cubic \rightarrow SmC)^[10] which would be a primary reason for the failure of miscibility between the CubD phase and the cubic phase^[2].
7. The "Alkyl-chains as Entropy reservoir" mechanism is identified as a new type of influences that modify the phase behavior of molecular system.

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