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THERMODYNAMIC IMPLICATION OF THE DEPENDENCE OF MESOMORPHIC TRANSITION ENTROPY ON CHAIN-LENGTH

Smectic A – nematic phase transition*

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Abstract

Meaning of the alkyl chain-length dependence of transition entropy in liquid crystal is discussed and clarified in a long-chain region. A method to deduce contributions of the alkyl chain and the molecular core is proposed. Application of the method suggests that, in most smectic A (SmA) – nematic (N) phase transitions, not only a molecular core (modeled by a hard-rod) but also a (terminal) alkyl chain is disordered upon the SmA→N transition.

Keywords: chain-length dependence, entropy of transition, liquid crystal, smectic A – nematic transition

Introduction

Theoretical modeling of liquid crystals goes back to the Onsager's paper in 1949 [1], where molecules are modeled by hard rods. Many succeeding theories also assume rigid bodies as molecules [2, 3]. Molecules of most mesogens, however, are not rigid but consist of a (semi)rigid core and flexible alkyl chain(s) as exemplified in Fig. 1. This situation has prevented reliable comparison between predictions by models and experimental results on thermodynamic quantities of transition.

In the course of study on thermotropics having optically isotropic mesophases of labyrinth structures [4–9], the present authors arrived at the 'binary picture' for the mesogens [4, 8]. Namely, the phase diagram of a given system is governed by the 'concentration' of paraffinic carbon atoms. Based on this binary picture, entropies of the chain and the molecular core were deduced from the chain-length dependence of the entropies of transition for some mesogens [7, 9] between smectic C (SmC) and isotropic mesophases with different space groups. Taking into account that in most

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cases mesogenic molecule has alkyl chains at least at its one end, this ‘binary picture’ deserves a further consideration.

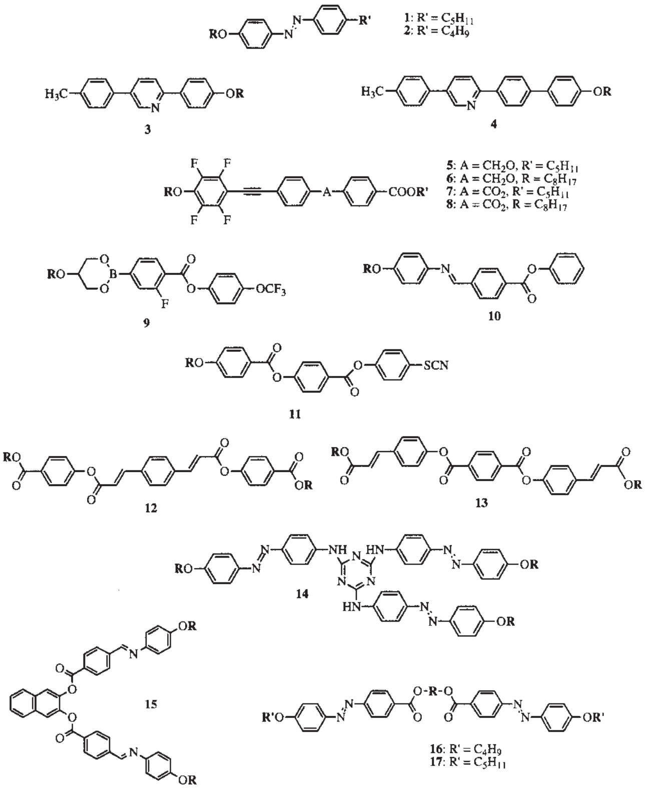

Fig. 1 Structures of mesogenic molecules. Alkyl and polymethylene chains are denoted by **R** and/or **R′**

In this paper, we propose a thermodynamic method to deduce the contributions of the chain and the rigid core. The core contribution may fit to direct comparison with rigid-rod models. On the other hand, the chain contribution itself is certainly of interest because the motional degrees of freedom of the chain are intramolecular by nature and beyond the scope of rigid-rod models. The logic and method described in this paper have already been certified to work quite well in the SmC↔isotropic mesophases with labyrinth structures [7–9], though its general nature has been stated only implicitly. In the present paper, the logic is explained while placing a special emphasis on its generality and applying to SmA–N transitions to shed light on the alkyl chain dynamics.

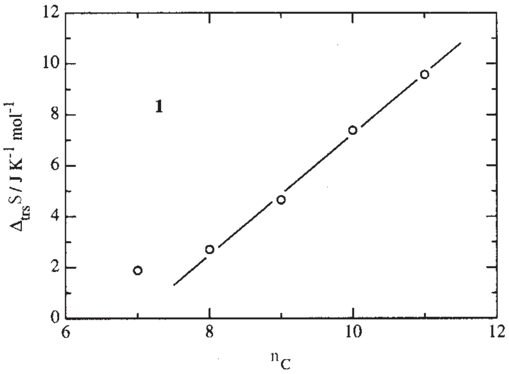

Fig. 2 Alkyl chain length dependence of the entropy of the SmA–N transition of compound **1**. Linear line is the assumed linear dependence

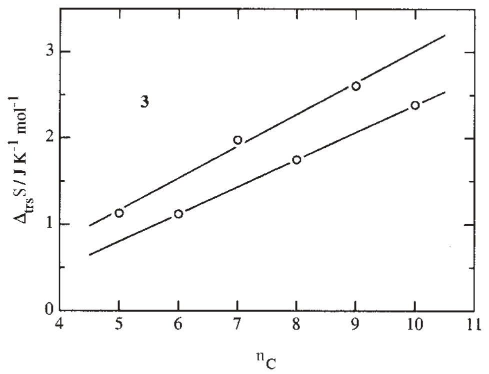

Fig. 3 Alkyl chain length dependence of the entropy of the SmA–N transition of compound **3**. Linear lines are the assumed linear dependence for odd and even members

Chain-length dependence of entropy of transition

If the absolute entropy of a given liquid crystalline phase is primarily determined by the arrangement of the rigid rods and by the resulting dynamical excitations, the entropy of transition is expected to be independent of the chain length. This is not true. For example, Fig. 2 shows the chain-length dependence of the entropy of the smectic A (SmA)→nematic (N) phase transition in compound **1** [10]. The plot shows a good linearity for n_C= 8–11 with a slope of 2.3 J K^{-1} mol^{-1}.

The compound **1** consists of a semirigid core and flexible chain as shown in Fig. 1. These 'components' will behave differently due to their different flexibility. We recall that entropy is an extensive quantity with a clear microscopic meaning (logarithm of the number of microscopic states). The entropy of transition, therefore, should depend linearly on the chain length for sufficiently long chains. The methylene group not far from the core part may reorient itself under the constraint of bonding to the core part while those at a distance behave nearly freely. It is often the case that properties such as temperature and entropy of phase transition exhibit a clear odd-even effect. For such a case, the chain-length dependence should be considered separately for odd and even members as shown in Fig. 3 for compound **3** [11]. It is emphasized that the above logic may equally be applied in any phase transitions of compounds having long chains.

The sign of the slope represents the disordering (+) or ordering (–) upon the phase transition. The slope itself is the difference in entropy per methylene in two phases. From the viewpoint of molecular dynamics in liquid crystals, this quantity is of great interest because the motional degrees of freedom of the chain are intramolecular in nature and beyond the scope of rigid-rods model. The present method of analysis is unique with respect to the time scale covered in study of chain dynamics. Spectroscopies such as NMR are widely used to study molecular dynamics. Each spectroscopic method has a characteristic time scale, by which the molecular dynamics is successfully sensed. The characteristic time scales of spectroscopies are generally equal to the inverse of the frequency used. For NMR, which is widely used and may be the most powerful method, it is 10^{-8}–10^{-10} s. On the other hand, as the present method is based on thermodynamics, the time scale is extremely long, just as sensed by our daily life. The characteristic time is about 10^3 s. Very slow dynamics, therefore, is favorably studied. Besides, this time scale of thermodynamics implies the slowest limit of molecular dynamics that can be detected. Fast dynamics (e.g., that detected by NMR) is also covered by the present method, though no information is available concerning the time scale of the dynamics. One may claim that the present method needs many compounds in a series of mesogen, exhibiting the mesophases under interest. This is true. It should be, however, pointed out that synthetic effort is also necessary for a comprehensive study by NMR, which is probably performed using molecules in which some atoms are site-selectively substituted by isotope [12].

The entropy of transition at a short-chain limit in the present analysis may be regarded as the core contribution because the present partition scheme is on a ‘real particle’ basis. The core size, therefore, may be different from the real size of the semirigid core part of molecule because methylenes not far from the core part reorient themselves under the constraint of bonding to the nominal core, and consequently, behave as a part of the core.

If the mesophase of interest survives in short-chain mesogens and the entropy of transition shows a tendency to converge to some value at the short-chain limit, the converged value corresponds to the contribution of the core, which may be directly compared with predictions by rigid-rod models. The dependence on the chain length shown in Fig. 2 is consistent with this expected behavior. The other way to deduce the core contribution is the estimation of the effective core size. This is possible through a study on a binary system between *n*-alkane and a short-chain mesogen for some cases [4]. Suppose the phase diagram is primarily governed by the number of paraffinic carbon atoms in the system as in the cubic mesogens showing optically isotropic mesophases with labyrinth structures [4, 8]. The mesophase of interest will be induced by adding *n*-alkane if a short-chain mesogen is longer than the effective core [4, 8, 13]. The longest-chain mesogen for which the mesophase of interest is not induced by such a treatment can roughly be regarded as the size of the effective core necessary for the mesophase. In our previous papers on the optically-isotropic mesophases with labyrinth structure [4, 7–9] such an estimate was successfully done and the contribution of the core was deduced.

There is a possibility that contributions of the molecular core and the chain compete each other. This really occurs in the phase transitions between a SmC phase and optically isotropic mesophases with labyrinth structures [7, 9]. Due to the competition in entropy contributions of the core and the chain, the phase sequence (with respect to temperature) may be inverted upon changing the chain length [7].

SmA–N transition

The SmA–N transition can be described by using rigid-rod models [3]. The loss of periodicity along the normal of a smectic layer due to thermal disordering is involved in a SmA→N transition upon heating. These models, however, tell nothing about the disorder of alkyl chain(s) attached to a molecular core for real mesogenic molecules, because the intramolecular dynamics and resulting disordering are beyond the scope of the models. It is noted that rigid-rod models are, in principle, applicable to systems consisting of flexible molecules because the molecular direction can be defined for such molecules unless the anisotropy is completely averaged out.

To deduce a trend of disordering/ordering upon the SmA–N transition, data reported in a journal Liq. Cryst. in the period 1993–1999 are compiled. Series of linear (calamitic) mesogenic compounds showing a SmA–N transition are selected, for which entropy of transition has been reported for three or more compounds in a series. Thirteen series of mesogenic compounds (**1**–**13** in Fig. 1) [10–19] fit to this criterion. The experimental entropies of SmA→N transition were fitted to a linear equation, though rather short chain compounds were also included in the fits due to limited numbers of available

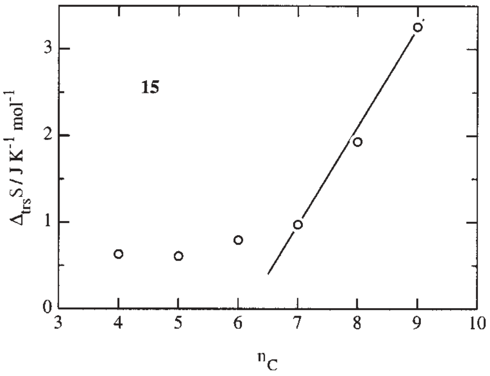

Fig. 4 Alkyl chain length dependence of the entropy of the SmA–N transition of compound **15**. Linear line is the assumed linear dependence

data (compounds) in a series.The results of analysis are summarized in Table 1. There seems to exist a tendency that the fit becomes bad if the core of mesogenic molecule becomes flexible (i.e., increasing positions where a molecule may bent, N in Table 1). All series show an increase in the entropy of transition with increasing n_C (number of carbon atoms in a chain).This suggests that, in most SmA–N phase transitions, not only the molecular core (modeled by a rigid-rod) but also the alkyl chain is disordered upon SmA–N transitions of linear mesogens. As to the magnitude of the slope, no universality is recognized in Table 1, in contrast to the case of the phase transition from the SmC to the optically isotropic mesophase with space group Ia3d [7, 8].

Table 1 Summary of the fits of experimental entropies of the SmA→N transition [$\Delta_{trs}S_{exp}$(SmA→N)] for n compounds in a series to $\Delta_{trs}S_{fit}=An_{para}+B$, where n_{para} is the number of paraffinic carbon atoms per molecule and may be different from the alkyl chain length n_C. Information on the residuals of the fit ($\Delta=\Delta_{trs}S_{exp}-\Delta_{trs}S_{fit}$) is also given. The molecule can be bent at N positions

Compound	A/J K^{-1} (mol of CH$_2$)$^{-1}$	n_C	$[\Sigma\Delta^2/(n-2)]^{1/2}$/ J K^{-1} mol^{-1}	n	N	Reference
1	2.33	8–11	0.22	4	1	10
2	3.00	8–11	1.24	4	1	10
3	0.32	6–10 (even)	0.00	3	0	11
3	0.37	5–9 (odd)	0.09	3	0	11
4	0.28	4–10	0.37	7	0	14
5	0.82	5–8	0.43	4	1	15
6	1.26	1–5	0.58	5	1	15
7	0.40	2–7	0.44	6	1	15
8	0.58	1–5	0.49	5	1	15
9	2.54	3–5	0.24	3	1	16
10	0.73	3–10	0.73	8	2	17
11	0.91	4–7	0.95	4	2	18
12	0.20	5–7	0.40	3	4	19
13	0.50	2–5	0.45	4	4	19
14	0.08	10–16	0.32	3	–	20
15	0.25	4–9	0.55	6	–	17
16	–0.45	4–8	0.49	3	–	21
17	–0.85	4–10	0.62	7	–	22

Mesogenic molecules having a non-linear core part also show SmA–N transitions. Two compounds (**14** and **15** in Fig. 1) are examples of such compounds [17, 20]. They also show a linear increase in the entropy of SmA–N transition with respect to the increase in length of the chain attached at molecular ends, as seen in

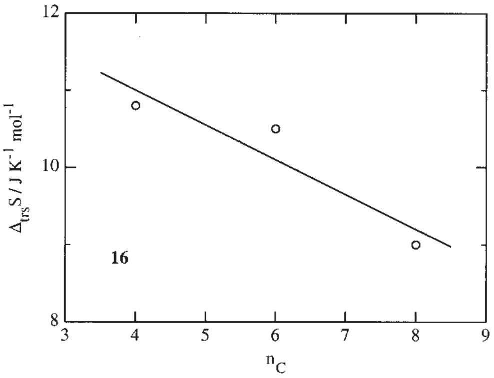

Fig. 5 Polymethylene chain length dependence of the entropy of the SmA–N transition of compound **16**. Linear line is the assumed linear dependence

Fig. 4 for compound **15** [17]. This suggests that the disordering upon SmA→N transition be a general tendency if alkyl chains are bonded at molecular end(s).

The present discussion on the entropy of transition may equally apply to mesogenic molecules having long alkyl chains even at the inner part of the molecule. Interestingly, dimeric mesogens **16** [21] and **17** [22] exhibit a decrease in the entropy of the SmA–N transition upon elongation of the chain as shown in Fig. 5 for **16**, though their polymethylene chains may be too short for the present analysis to work well. It is also noteworthy that the asymmetric dimers (with different alkyl chains at molecular ends) behaves differently [22].

Conclusions

Implication of the alkyl chain-length dependence of transition entropy in liquid crystal is discussed and clarified. A method to deduce contributions of the alkyl chain and the molecular core is proposed and its merit/demerit is discussed in comparison with spectroscopies. The method is applied to the SmA–N transitions. Not only a molecular core but also an alkyl chain is disordered upon the SmA→N transition in most SmA–N phase transitions of mesogens having chain(s) at the molecular end(s). A bridging polymethylene chain in a dimeric mesogen is suggested to play a different role from those at molecular end(s) on SmA–N transition.

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