

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### **Towards the molecular-statistical modelling of the optically isotropic mesophase in neat systems: from the thermodynamic point of view**

Kazuya Saito<sup>a</sup>; Takashi Shinhara<sup>a</sup>; Michio Sorai<sup>a</sup>

<sup>a</sup> Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan,

Online publication date: 06 August 2010

**To cite this Article** Saito, Kazuya , Shinhara, Takashi and Sorai, Michio(2000) 'Towards the molecular-statistical modelling of the optically isotropic mesophase in neat systems: from the thermodynamic point of view', *Liquid Crystals*, 27: 11, 1555 – 1559

**To link to this Article:** DOI: 10.1080/026782900750018744

**URL:** <http://dx.doi.org/10.1080/026782900750018744>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Towards the molecular-statistical modelling of the optically isotropic mesophase in neat systems: from the thermodynamic point of view†

KAZUYA SAITO\*, TAKASHI SHINHARA and MICHIO SORAI

Research Center for Molecular Thermodynamics, Graduate School of Science,  
Osaka University, Toyonaka, Osaka 560-0043, Japan

(Received 24 March 2000; in final form 26 May 2000; accepted 15 June 2000)

Phase diagrams of some compounds showing optically isotropic mesophases are compared as a function of the number of paraffinic carbon atoms per molecular core. In spite of a wide range of the transition temperatures, the number of paraffinic carbon atoms required for the appearance of the isotropic mesophases is limited within a narrow range, irrespective of molecular structure and/or intermolecular interaction. Combining this finding with the previous results obtained from thermodynamic studies, a possible framework towards molecular-statistical modelling is proposed.

For a long time, compounds showing optically isotropic mesophases were limited to those designated as ANBC(*n*) (1: 4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acids, *n* in parenthesis being the number of carbon atoms in the alkoxy chain) [1–3], ACBC(*n*) (2: 4'-*n*-alkoxy-3'-cyano-biphenyl-4-carboxylic acids) [3] and BABH(*n*) [3: 1,2-bis-(4-*n*-alkoxybenzoyl)hydrazines] [4, 5]. Nowadays, however, many compounds are known to exhibit isotropic phases [6–11], and molecular structures of the cubic mesogens involved in this communication are shown in figure 1. The structures and properties of the isotropic phases have gradually become of general interest. Although X-ray diffraction studies have established space groups for some isotropic phases [12], even in these cases, there is no definite structural model on the molecular level. It is, therefore, urgent to elucidate the isotropic phase at the molecular level.

It is known that similar morphologies are observed in lyotropic liquid crystals and block copolymers. Extensive theoretical treatments based on the properties of the surface (interface) formed there have been made [13, 14]. What corresponds to the assumed surface is clear (or trivial) for them; a bilayer formed by surfactant in the former case and an interface in the 'phase separation' in the latter. Although similar (or even the same) morphologies suggest that such treatments are

applicable to the isotropic mesophases in the neat systems, the correspondence is unclear. Molecular models of the isotropic mesophases in the neat systems would enable us to imagine what occurs in this exotic aggregation state and how it occurs, and consequently deepen our understanding of it.

In previous studies on ANBC(*n*) and BABH(*n*) [15–19], we have shown some important characteristics from the aspect of thermodynamics. Those relevant to the following discussion can be summarized as follows:

- The cubic mesogens commonly exhibit marked solid–solid phase transitions [16–18]. 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.
- This highly disordered alkoxy chain in the isotropic mesophase behaves like a solvent in lyotropic systems [15].
- The terminal alkoxy chains are more disordered in the isotropic mesophases ( $0.5 \text{ J K}^{-1} \text{ CH}_2^{-1}$  in terms of entropy) than in the neighbouring SmC phase, whereas the spatial arrangement of the molecular core is more ordered in the isotropic phase than in the SmC phase by  $(1 \pm 0.5) R$  ( $R = \text{gas constant}$ ) in terms of entropy [18].
- The isotropic phases of ANBC and BABH may be identical in nature in spite of their different phase sequences (on heating, SmC → CubD in ANBC and Cubic → SmC in BABH) [18].

\* Author for correspondence

e-mail: kazuya@chem.sci.osaka-u.ac.jp

† Contribution No. 20 from the Research Center for Molecular Thermodynamics.

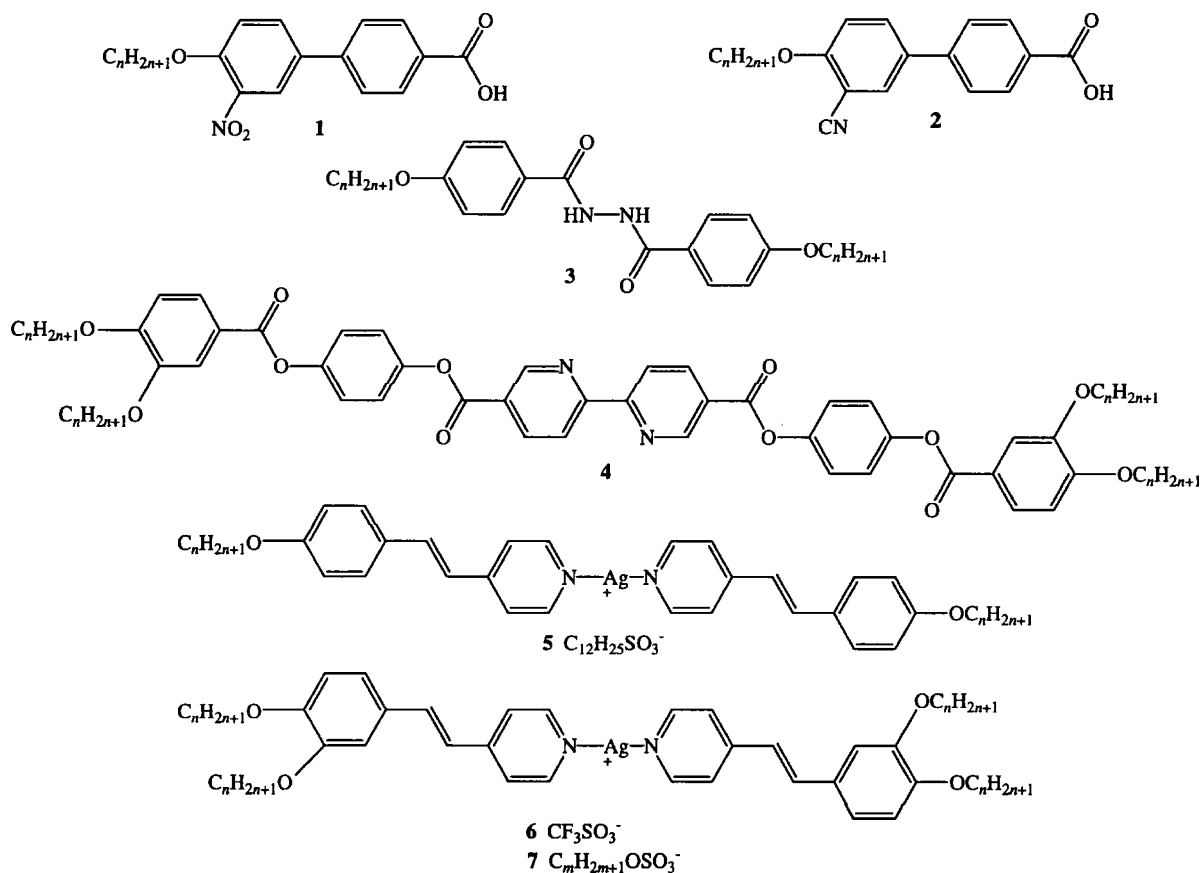


Figure 1. Structure of ANBC(*n*) (1), ACBC(*n*) (2), BABH(*n*) (3), a tetracatenar (four chain) bipyridine (4), [Ag(4-alkoxystilbazole)<sub>2</sub>] $C_{12}H_{25}SO_3^-$  (5), [Ag(3,4-dialkoxystilbazole)<sub>2</sub>] $CF_3SO_3^-$  (6) and [Ag(3,4-dialkoxystilbazole)<sub>2</sub>] $C_mH_{2m+1}OSO_3^-$  (7).

(e) The inverted phase sequence results from the competing contribution of the chain and molecular core to the entropy of transition. The ‘alkyl-chains as entropy reservoir’ mechanism is identified as a new type of influence that modifies the phase behaviour of molecular systems [18, 19].

As exemplified in figure 1, most compounds showing the isotropic mesophases have a similar molecular structure. That is, the molecules consist of a rather rigid core at the centre and some flexible alkyl chains, forming a very symmetrical structure. It may be necessary to make a comment on ANBC (1) and ACBC (2). In the mesomorphic phases, the ANBC (and probably ACBC) molecules form carboxylic acid dimers through hydrogen bonding [20, 21]. It is not clear at present whether a dimerized or dimeric type structure, common for all the molecules in figure 1, is necessary for the appearance of the isotropic phases. Another similarity in the molecular structures can be recognized: the molecular core commonly possesses some sites that offer interaction in the lateral direction. These similarities naturally lead us to suspect common physical properties. The identification

of these common properties will greatly help in proposing a framework of the molecular model of the isotropic phase. It is emphasized that the present purpose is *not* to find common factors governing the appearance of *all* known cubic phases, but to extract the characteristics of a group of cubic mesogens. In this respect, it is clear to us that exceptional systems exist and do not fit the following discussion. However, to concentrate attention on some common characteristics, even though they are not common for *all* known systems, could be the way to obtain new ideas. For exceptional systems, more extensive and detailed treatments could follow the simple framework suggested in this paper.

In a previous paper [15], we showed that the phase diagram of ANBC is essentially governed by the number of the paraffinic carbon atoms within the system through a study of ANBC-*n*-alkane binary systems. It is quite interesting to see whether this holds for other compounds. The selected compounds [7–11, 21] shown in figure 1 cover a variety of combinations of molecular structure and intermolecular interaction: the size of the molecular core varies (4 and others); the number of alkyl

chains attached to the molecular core is two (**1** and **5**) or four (**4**, **6** and **7**); the paraffinic carbon atoms are attached directly to the core (**1**, **4** and **6**) or supplied from the counter anion (**5** and **7**); the core is either a single unit (**4–7**) or a dimer formed through hydrogen bonding (**1**). Finally, the intermolecular interaction may be a simple hydrogen bond, a dipolar interaction (**1**), or Coulombic interactions mediated by counter ions (**4–7**).

The finding (c) mentioned above holds for the compound **5** [7] as seen in figure 2, though the data are slightly scattered. Here  $n_c$  is the number of the paraffinic carbon atoms per molecular core; that is, it is the number of chains attached to the core (2 or 4)  $\times$  the chain length + the number of carbon atoms within the counter anion (if applicable). Since the entropy of transition from the SmC phase to the isotropic phase of **5** increases linearly, the paraffinic carbon atoms are in a more disordered state in the isotropic phase than in the SmC phase. An extrapolation to  $n_c = 0$  gives an estimate of the entropy of transition assignable to the spatial arrangement of the molecular core. As clearly seen from figure 2, this entropy contribution is negative. The entropy contribution by a paraffinic carbon atom in **5** is roughly the same as those in **1** and **3**, as discussed previously [18]. This strongly suggests that the isotropic mesophases of the neat compounds are, at least from a thermodynamic point of view, the same or quite similar to one another. A detailed discussion concerning the plot shown in figure 2 has been given in a previous paper [18].

Figures 3–7 show the  $n_c$ - $T$  phase diagrams for compounds **1** [22] and **4–7** [7–11]. Here Col<sub>h</sub> denotes a hexagonal columnar mesophase. The phase diagrams are

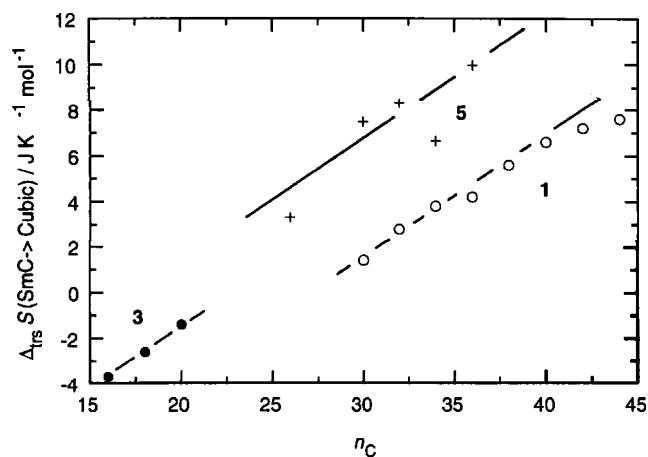


Figure 2. Entropy of transition from the SmC phase to the isotropic (cubic) mesophases as a function of  $n_c$ . Open circles, **1** (ANBC); closed circles, **3** (BABH); plus sign, **5**. Due to the dimerization through hydrogen bonds the value of  $n_c$  is twice the chain length of **1**.

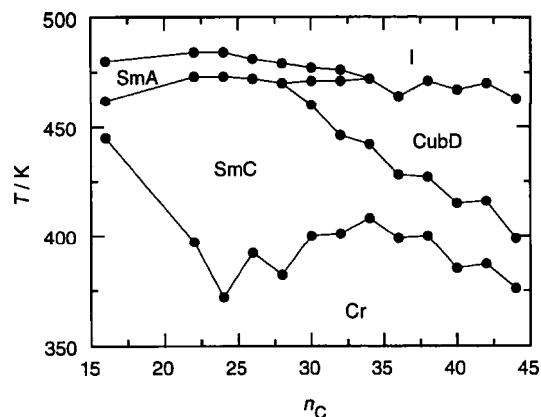


Figure 3.  $n_c$ - $T$  phase diagram of ANBC (**1**).

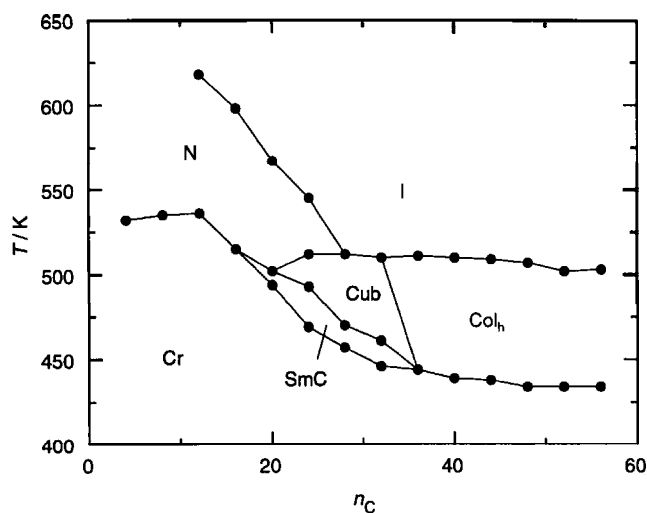


Figure 4.  $n_c$ - $T$  phase diagram of **4**.

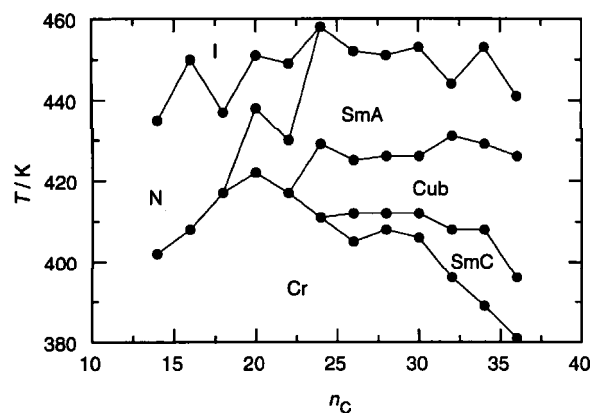


Figure 5.  $n_c$ - $T$  phase diagram of **5**.

generally similar in spite of the wide range of transition temperatures. This implies that the phase diagrams of these systems are essentially determined by geometrical factors.

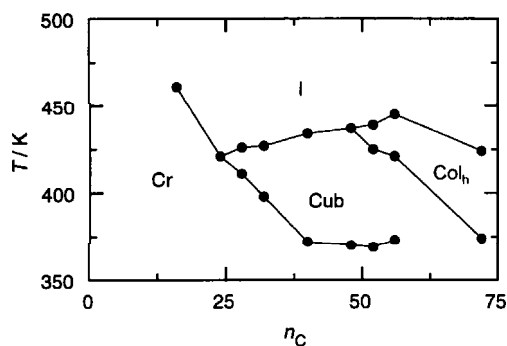


Figure 6.  $n_C$ - $T$  phase diagram of 6.

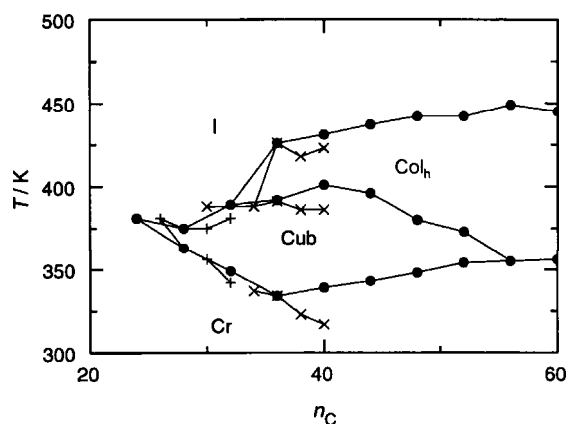


Figure 7.  $n_C$ - $T$  phase diagram of 7. The filled circles represent the case where  $n$  varies with  $m = 12$ . The plus signs and crosses are for the cases where  $m$  varies with  $n = 4$  and 6, respectively.

A point to be emphasized is that, in spite of the wide variety of systems, the lower critical carbon number required for the isotropic phases lies in a rather narrow range around 25. These facts suggest that the phase diagrams of these compounds depend primarily on the number of the paraffinic carbon atoms in the system, and only weakly on the details of the system such as the molecular structure, location of the paraffinic carbon atoms or the intermolecular interactions. The existence of the lower critical number implies that a certain amount of paraffinic carbon is necessary for the appearance of the isotropic phase. On the other hand, the presence of an upper critical number is seen in some cases. These facts suggest strongly that an optimum range of paraffinic carbon atom content exists for stabilization of the isotropic phase. Although not much is known for ACBC (2), the available information [3] is compatible with these findings.

Figure 7 displays an interesting feature for the compounds 7 [10], where two kinds of phase diagrams are superimposed. One is a phase diagram for the change in length of the chain directly attached to the molecular core while keeping the counter anion identical, whereas

the other is the phase diagram for the change in the chain length of the counter anion while keeping the cation identical. The coincidence between the two kinds of phase diagram is almost perfect. This indicates that the location and nature of the paraffinic carbon atoms has only a secondary influence on the phase diagram. This is fully consistent with our previous conclusion (b) [15].

The phase behaviour of BABH (3) has a different character from those described above. The cubic phase of BABH appears in the range  $16 \leq n_C \leq 20$  [4, 5], values which are smaller than those given above. The core of the BABH molecule is also smaller than those of others. Besides, the cubic phase of BABH is located on the low temperature side of the SmC phase, while other isotropic phases discussed above appear on the high temperature side. This inversion in the phase sequence results from the small entropy contribution of the chain [18, 19], and the stable region of the isotropic phase is therefore considered to cover the case of BABH.

Now we summarize our findings and suggest a guideline for constructing a molecular-statistical model of the isotropic phase, while concentrating our attention on the phase transition between the cubic and SmC phases. Since the difference in entropy of the chain is small (though this difference does determine the phase sequence) [18, 19], we may assume that the chain acts as a continuum to fill the voids produced in the higher order structure of the cores, as a zeroth approximation. The system to be considered thus consists of the hard rod-like cores and the space-filling fluid [15, 18, 19]. The volume fraction must be selected to match the experimental phase diagram shown in figures 2–6. The hard cores attract each other in a lateral direction as seen from figure 1. The nature of the interaction, such as of long or short range forces, is unimportant as we have shown here. If some phases with cubic higher order structures have a smaller entropy than the SmC phase by about  $R$ , they are possible candidates for the isotropic mesophase experimentally observed [18]. Of course, the cubic structure(s) must not contradict existing information concerning the space groups of the isotropic phases. The next step is to include the entropy of the fluid, which will determine the phase sequence [18, 19].

A short comment is in order concerning the thermodynamic location of the  $Col_h$  phase with respect to the isotropic phase. Figure 8 shows the entropy of transition from the cubic phase to the  $Col_h$  phase of 7 [8] as a function of  $n_C$ . The  $n_C$  dependence is weak, implying a comparable disorder of the alkyl chains. If a line is tentatively drawn, ignoring the data corresponding to  $n_C = 36$ , the slope is negative. The negative slope suggests that the chain is slightly more disordered in the cubic phase than in the  $Col_h$  phase. A more important point

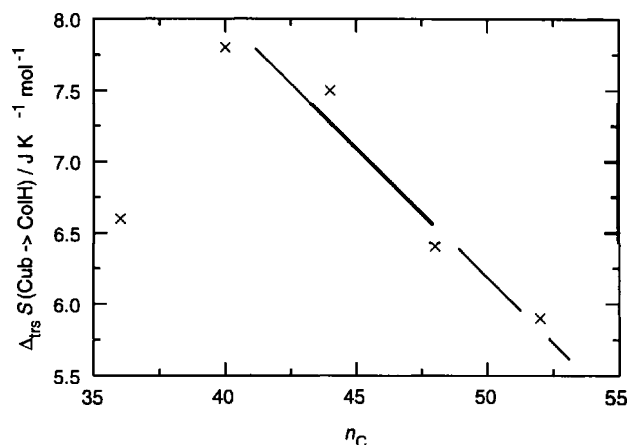


Figure 8. Entropy of transition from the cubic phase to the  $\text{Col}_h$  phase as a function of  $n_C$  for 7 with  $m = 12$ .

is the positive contribution is to be assigned to the molecular core. That is, the  $\text{Col}_h$  phase seems to be more disordered than the cubic phase with respect to the spatial arrangement of the core by about  $10 \text{ J K}^{-1} \text{ mol}^{-1}$  in terms of entropy. It is dangerous to develop too detailed a discussion based upon only one plot, but we believe that the analysis based on plots of entropy of transition against  $n_C$  or chain length [17] does allow us to deepen our molecular understanding of liquid crystalline states.

In this communication, we have outlined the thermodynamic requirement of the molecular model for isotropic mesophases in neat systems. We hope that this outline stimulates further theoretical studies.

### References

- [1] GRAY, G. W., JONES, B., and MARSON, F. F., 1957, *J. chem. Soc.*, 393.
- [2] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals—Textures and Structures* (Glasgow and London: Leonard Hill), Chap. 4 and references therein.
- [3] DEMUS, D., KUNICKE, G., NEELSEN, J., and SACKMANN, H., 1968, *Z. Naturforsch.*, **23**, 84.
- [4] SCHUBERT, H., HAUSCHILD, J., DEMUS, D., and HOFFMANN, S., 1978, *Z. Chem.*, **18**, 256.
- [5] DEMUS, D., GLOZA, A., HARTUNG, H., HAUSER, A., RAPTHEL, I., and WIEGEBEN, A., 1981, *Cryst. Res. Technol.*, **16**, 1445.
- [6] DIELE, S., and GÖRING, P., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), Chap. XIII.
- [7] BRUCE, D. W., DUNMER, D. A., HUDSON, S. A., LALINDE, E., MAITLIS, P. M., McDONALD, M. P., ORR, R., and STYRING, P., 1991, *Mol. Cryst. liq. Cryst.*, **206**, 79.
- [8] DONNIO, B., HEINRICH, B., GULIK-KRYWICKI, T., DELACROIX, H., GUILLON, D., and BRUCE, D. W., 1997, *Chem. Mater.*, **9**, 2951.
- [9] ROWE, K. E., and BRUCE, D. W., 1998, *J. mat. Chem.*, **8**, 331.
- [10] DONNIO, B., and BRUCE, D. W., 1998, *J. mat. Chem.*, **8**, 1993.
- [11] DONNIO, B., and BRUCE, D. W., 1999, *New J. Chem.*, 275.
- [12] For example, LEVELUT, A.-M., and CLERC, M., 1998, *Liq. Cryst.*, **24**, 105.
- [13] For an example on lyotropic systems see SCHWARZ, U. S., and GOMPPER, G., 1999, *Phys. Rev. E*, **59**, 5528.
- [14] For an example on copolymers see BENEDICTO, A. D., and O'BRIEN, D. F., 1997, *Macromolecules*, **30**, 3395.
- [15] SAITO, K., SATO, A., and SORAI, M., 1998, *Liq. Cryst.*, **25**, 525.
- [16] MORIMOTO, N., SAITO, K., MORITA, Y., NAKASUJI, K., and SORAI, M., 1999, *Liq. Cryst.*, **26**, 219.
- [17] SAITO, A., SAITO, K., and SORAI, M., 1999, *Liq. Cryst.*, **26**, 341.
- [18] SAITO, A., YAMAMURA, Y., SAITO, K., and SORAI, M., 1999, *Liq. Cryst.*, **26**, 1185.
- [19] SAITO, K., SAITO, A., MORIMOTO, N., YAMAMURA, Y., and SORAI, M., 2000, *Mol. Cryst. liq. Cryst.* (in the press).
- [20] KUTSUMIZU, S., KATO, R., YAMADA, M., and YANO, S., 1998, *J. phys. Chem. B*, **101**, 10666.
- [21] TANSHO, M., ONODA, Y., KATO, R., KUTSUMIZU, S., and YANO, S., 1998, *Liq. Cryst.*, **24**, 525.
- [22] KUTSUMIZU, S., YAMADA, M., and YANO, S., 1994, *Liq. Cryst.*, **16**, 1109.