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## Liquid Crystals

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# Temperature-dependent FTIR study of a supramolecular mesophase from the self-assembly of melamine and barbituric acid derivatives

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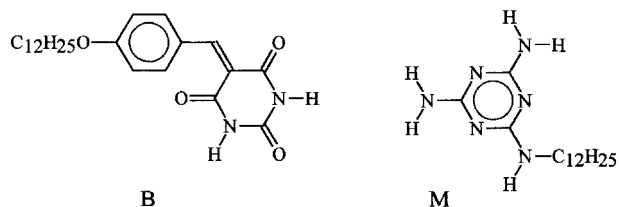
A supramolecular mesophase was prepared from molecular recognition directed self-assembly of two complementary molecular components, namely 5-(4-dodecyloxybenzylidene)-2,4,6-(1H,3H)-pyrimidinetrione and 4-amino-2,6-didodecylamino-1,3,5-triazine. Differential scanning calorimetry measurements indicate a mesophase having liquid crystalline properties. Infrared studies suggest that not only hydrogen bonds but also  $\pi$ -aromatic stacking and van der Waals interactions direct the formation of the mesophase.

## 1. Introduction

Non-covalent bonds or interactions are universally used by biological systems to assemble molecules and now employed widely in the design and synthesis of new types of functional supramolecular materials [1–3]. Among them hydrogen bonds have received more attention than other weak and non-directional interactions, such as van der Waals,  $\pi$ -aromatic stacking, hydrophobic, etc., due to their strong and directional nature. There have been many successful examples of fabricated hydrogen bond-induced liquid crystalline phases [4–8]. In biological systems, however, more than one kind of non-covalent bond or interaction may be used to obtain a final ordered, complex structure and this suggests that combination of bonds or interactions may provide new possibilities for the preparation of supramolecular materials with novel structures and properties.

To mediate intermolecular interactions besides hydrogen bonds, we have designed and synthesized a new series of complementary molecular components, amphiphilic melamine and light active barbituric acid derivatives [9]. It was found that a nanofilamentary mesophase [10] was formed through molecular recognition directed self-assembly between 5-(4-dodecyloxybenzylidene) barbituric acid (**B**) and 4-amino-2,6-didodecylamino-1,3,5-triazine (**M**), and more than 1,200 h were necessary for this process of self-assembly to reach equilibrium [11]. This suggests that not only hydrogen bonds, but also other non-covalent interactions, directed the formation of the mesophase since the process of

hydrogen bond directed self-assembly generally is a fast one. Here we try to examine these materials by infrared spectroscopy since this can provide useful information on intermolecular non-covalent interactions [12].



## 2. Experimental

The syntheses of the melamine and barbituric acid derivatives have been reported in detail elsewhere [9]. The two complementary molecular components used in this study are 5-(4-dodecyloxybenzylidene)-2,4,6-(1H,3H)-pyrimidinetrione (**B**) and 4-amino-2,6-didodecylamino-1,3,5-triazine (**M**). The resulting supramolecular mesophase (**B**·**M**) was obtained as a yellow precipitate after **B** was mixed with one equivalent of **M** in chloroform for more than 50 d. The precipitate was dried under vacuum at 40°C. DSC (differential scanning calorimetry) measurements were conducted using a Perkin-Elmer DSC7 with a heating rate of 10°C min<sup>-1</sup>. Infrared spectra were recorded with a Nicolet-5DX FTIR spectrometer equipped with a hot stage at a heating rate of 5°C min<sup>-1</sup> from 25°C to 180°C, with a maximal resolution of 2 cm<sup>-1</sup> over the entire range. KBr pellets were used for the measurements.

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### 3. Results and discussion

The DSC curves of **B**, **M** and **B·M** are shown in figure 1. It shows that both **B** and **M** are not mesogenic but the resultant **B·M** is a mesogen. This suggests the occurrence of intermolecular non-covalent interactions between **B** and **M** which result in the formation of the mesophase. No satisfactory textures could be observed through the polarized optical microscope, although the DSC curve indicates that it should exhibit liquid crystallinity, i.e. the latent heats are typical of LC transitions. The thermal transitions and thermodynamic parameters of **B·M** are summarized as follows:

$$\text{Cr (crystal state)} \xrightarrow[46.30 \text{ J}_g^{-1}]{127.3^\circ\text{C}} \text{LC}_1 \text{ (liquid crystal 1)}$$

$$\xrightarrow[3.79 \text{ J}_g^{-1}]{172.9^\circ\text{C}} \text{LC}_2 \text{ (liquid crystal 2)} \xrightarrow[5.50 \text{ J}_g^{-1}]{196.3^\circ\text{C}} \text{I (isotropic)}$$

The temperature-dependent IR spectra of **B·M** in the carbonyl stretching region are given in figure 2. The spectrum at 25°C shows carbonyl stretching bands at 1675, 1721 and 1737 cm<sup>-1</sup>. Before **B** and **M** were mixed, the carbonyl stretching bands of **B** were at 1668, 1727 and 1754 cm<sup>-1</sup> which were assigned to 2-carbonyl,

4,6-carbonyl symmetric and antisymmetric stretches, respectively [13]. These spectral changes suggest the formation of triply complementary hydrogen bonds between **B** and **M** [14]. This conclusion has also been supported by the spectral changes in the N–H stretching region [15] and that of the triazine ring vibration of **M** at 810 cm<sup>-1</sup> which is weakened significantly after **M** was mixed with **B** [14]. It has been well documented that three kinds of ribbon, cyclic hexamer, linear and crinkled oligomers, could be formed if triply complementary hydrogen bonds were formed between melamine and barbituric acid derivatives [16]. Here, the most favourable ribbon should be the cyclic hexamer since it can allow the sterically demanding substituents on adjacent molecules to get as far away as possible from each other (see figure 3).

At increased temperatures, it can be seen that the strength of the band at 1675 cm<sup>-1</sup> decreased greatly when the temperature reached 140°C. Changes of strength of the band intensities at 1721 and 1737 cm<sup>-1</sup> only occurred at the highest temperature, 180°C (see figure 2). This is reasonable since the 4,6-carbonyl moiety, whose stretches appear at a higher frequency, is a stronger proton acceptor than the 2-carbonyl group.

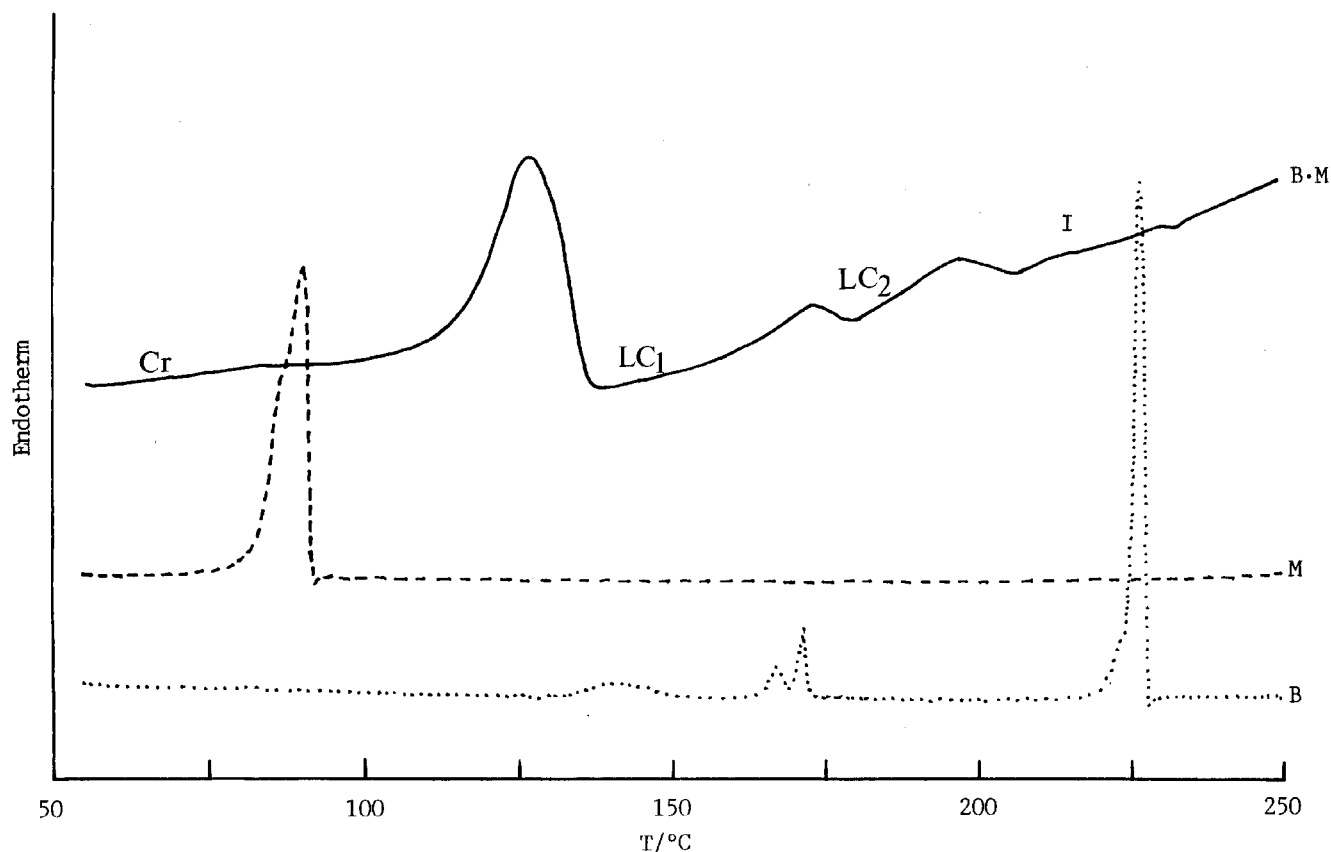


Figure 1. DSC curves of **B**, **M** and the supramolecular mesophase (**B·M**) recorded on the heating cycle.

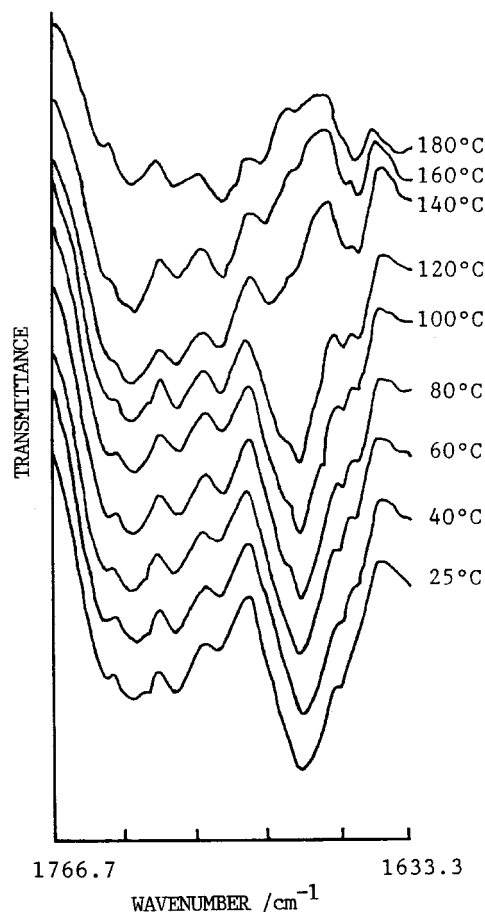


Figure 2. Temperature-dependent IR spectra of **B•M** in the region 1633.3–1766.7  $\text{cm}^{-1}$ .

These results mean that there have been changes of the hydrogen bonding at the crystalline–liquid crystal phase transition. In the  $\text{LC}_1$  phase only hydrogen bonds related with the 2-carbonyl moiety were weakened, and in the  $\text{LC}_2$  phase hydrogen bonds related with the 4,6-carbonyl group were also weakened.

Compound **B** shows a wide band at  $832\text{ cm}^{-1}$  assigned to C–H out-of-plane deformation  $\gamma(\text{CH})$  of the phenyl ring. In **B•M** this band became narrow and appeared at  $835\text{ cm}^{-1}$ . This indicates that the arrangement of the benzyl rings in **B•M** is more ordered than in **B** alone due to the stronger interactions between the conjugated parts of **B** in **B•M** [12]. We have known that hydrogen bond-induced self-assembly between **B** and **M** has resulted in the formation of the cyclic hexamer (see figure 3). Thus, we can conclude that there may exist strong interactions between the hexamers, and such interactions will assemble the hexamers into a layered structure as shown in figure 3. This is consistent with our X-ray diffraction pattern which suggests the mesophase shows a typical layered structure with a  $d$  value of  $4.1\text{ \AA}$  [10],  $0.7\text{ \AA}$  fewer than ( $4.8\text{ \AA}$ ) when two cyclic hexamers from molecular components preorganized by ‘hub’ and ‘spokes’ assembled into complex structures containing two parallel layers [16]. Hence, we can conclude that  $\pi$ -aromatic stacking interactions occur between the hexamers due to the introduction of the electron donor at the 5-position of the barbituric acid group in **B** which can increase the electron density of the conjugated part [17]. This  $\pi$ -aromatic stacking interaction can overcome the entropic cost of assembling the cyclic hexamers into a layered structure and result

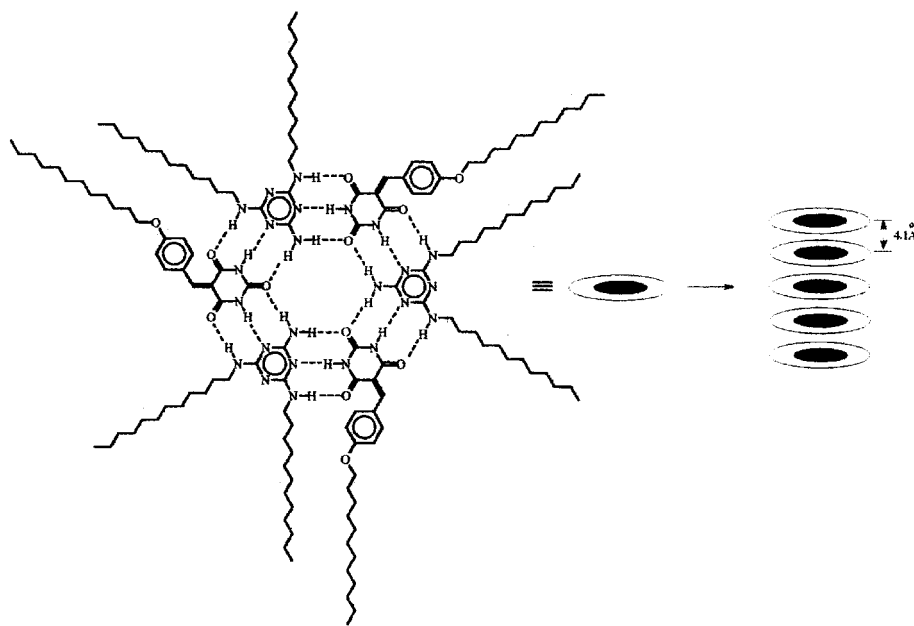


Figure 3. Schematic representation of the cyclic hexamers based on networks of hydrogen bonds between **B** and **M** and assembled into a columnar mesophase.

in the formation of a columnar mesophase (see figure 3), and this has been supported by our AFM observations which show the resultant self-assembly display morphology of nanofilaments with a length of several tens of  $\mu\text{m}$ , and a diameter of about 80 nm [10]. Temperature-dependent IR spectra show the band at  $835\text{ cm}^{-1}$  in **B**•**M** becoming weaker and wider when the temperature was raised to  $140^\circ\text{C}$  (see figure 4). This means that the interactions between the conjugated parts of the cyclic hexamers were weakened and the molecules became mobile when the mesophase experienced the transition from the crystalline state to the  $\text{LC}_1$  phase [12]. At the highest temperature,  $180^\circ\text{C}$ , this band became very weak which indicates that the alignment of the hexamers in the mesophase became less ordered in the  $\text{LC}_2$  phase.

The IR spectra of **B**•**M** in the C–H stretching region show methylene stretching modes  $\nu_a(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  at  $2920$  and  $2850\text{ cm}^{-1}$ , which are different from those observed for **B** ( $2920$  and  $2854\text{ cm}^{-1}$ ) and **M** ( $2921$  and  $2854\text{ cm}^{-1}$ ) alone. This indicates that the alignment of the aliphatic chains is more ordered in **B**•**M** than that in **B** and **M** alone [18]. The IR spectra in the  $\text{CH}_2$

deformation region also give rise to the same conclusion. In the IR spectrum of **B**•**M**, two peaks were observed at  $1464$  and  $1468\text{ cm}^{-1}$  which cannot be observed together in **B** and **M** alone. It is known that this splitting of  $\gamma(\text{CH}_2)$  is caused by the crystal field and is characteristic of *n*-paraffins which crystallize with orthorhombic subcell packing of  $\text{CH}_2$  groups. This means that the van der Waal's interactions between the aliphatic parts of **B** and **M** also contribute to the assembly of the cyclic hexamers into the columnar mesophase. The splitting observed here is lower than those in other cases [19] which can be explained by the weaker crystal field due to the low density of the aliphatic chains in the mesophase (see figure 3). The temperature-dependent IR spectra of **B**•**M** in the  $\text{CH}_2$  deformation region (see figure 5) show the alignment of the aliphatic parts experienced an order–disorder transition when the mesophase changed from the Cr to the  $\text{LC}_1$  phase. The variation of the frequency of  $\nu_a(\text{CH}_2)$  with temperature also lead to the same conclusion (see figure 6) [20]. However, at this time, the alignment of the rigid cores of the hexamers are still ordered (see figure 4).

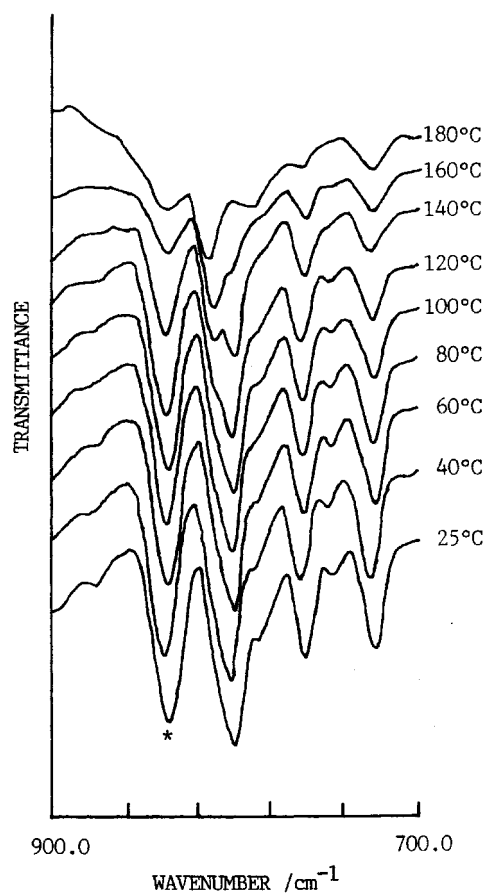


Figure 4. Temperature-dependent IR spectra of **B**•**M** in the range  $700\text{--}900\text{ cm}^{-1}$ .

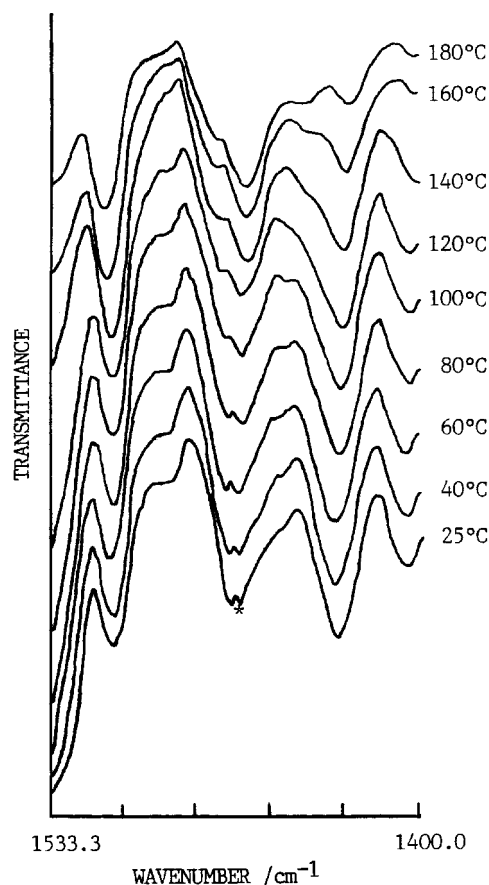


Figure 5. Temperature-dependent IR spectra of **B**•**M** in the range  $1400\text{--}1533.3\text{ cm}^{-1}$ .

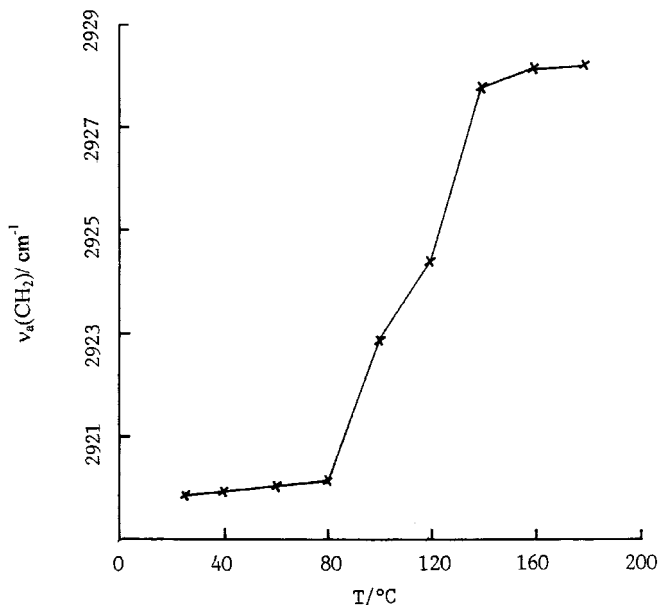


Figure 6. Variations of the frequencies of  $\nu_a(\text{CH}_2)$  with temperatures in the range 25–180°C.

In summary, the non-covalent interactions, which direct the formation of a supramolecular mesophase from self-assembly of **B** and **M**, have been investigated by FTIR spectroscopy. It can be deduced from the present investigation that besides complementary hydrogen bonds,  $\pi$ -aromatic stacking and van der Waal's interactions also direct the formation of the mesophase and are related to the phase transition behaviour of the mesophase. These results will provide new aspects in the design and build of supramolecular mesophases based on intermolecular non-covalent interactions.

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