Supramolecular Liquid Crystals with Hydrogen-Bonding Self-Assembled T-Shaped Mesogens

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A new class of supramolecular liquid crystals with T-shaped mesogens are obtained by doubly hydrogen-bonded self-assembly of 2,6-bis(4-hexyloxybenzoylamino)pyridine and benzoic acid derivatives.

In the conventional liquid crystals, the mesogenic units usually have the shape of rod-like(calamitic) or disc-like(discotic). The X-shaped or T-shaped mesogens were also reported in polymeric liquid crystals.[1,2] In supramolecular liquid crystals self-assembled by non-convalent interactions, there have been many examples in calamitic liquid crystals from hydrogen-bonding extended mesogens,[3] and discotic hydrogen-bonding associated mesogens from triazines and carboxylic acids which exhibited columnar liquid crystalline (LC) behavior were also reported.[4] It had been extensively demonstrated by Hamilton et al.[5,6] that double hydrogen bonds were formed by complexation between a 2-aminopyridyl and a carboxylic acid, and based on this type of doubly hydrogen-bonding, Kato et al. have built a series of supramolecular liquid crystals.[7–10] The 1:1 complexes of 2,6-bis(acylamino)pyridines with alkoxybenzoic acid showed monotropic LC behavior,[7] while the supramolecular complexes of 2,6-bis(acylamino)pyridines and azo mesogenic compounds containing carboxyl-terminated alkyl chains exhibited thermally stable enantiotropic LC behavior.[8] In all these examples, the LC units were long-alkyl chains modified calamitic mesogens. We report here a new class of supramolecular liquid crystals with hydrogen-bonded T-shaped mesogens. The aminopyridine-containing hydrogen-bonding component 2,6-bis(4-hexyloxybenzoylamino)pyridine (**1**) has been selected to form supramolecular complexes[11] with benzoic acid derivatives such as 4-methoxybenzoic acid (**2a**), 4-hexyloxybenzoic acid (**2b**) and 4-(4-methoxybenzoyloxy)benzoic acid (**2c**)[12]. Compound **1** was prepared from 2,6-diaminopyridine and hexyloxybenzoyl chloride. It was a white crystalline solid with only one sharp peak at 170.8 °C in the DSC heating run and at 160.7 °C upon cooling. ^{1}H NMR for **1**($CDCl_3$, 25 °C, ppm): 8.25, 8.22, 8.00, 7.80, 6.88, 3.95, 0.92–1.89. Phase transitions of the solid samples of molecular complexes were examined by DSC and visual observation on polarized optical microscope.

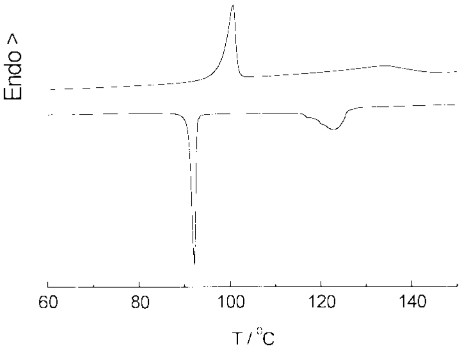

Figure 1. DSC thermogram of the complex **1/2b**.

DSC curves for the complex **1/2b** in heating and cooling runs are shown in Figure 1. It is noteworthy that the complex behaves as a single species and no transition duo to either of **1** and **2b** is observed for the mixture. The thermogram for **1/2c** is similar to that of **1/2b** in form of transition peaks except with different temperatures. Both of the complexes **1/2b** and **1/2c** show the enantiotropic LC characters. While the complex **1/2a** melts sharply to an isotropic state at 133.3 °C on heating, and upon cooling, two exothermic peaks which can be ascribed to isotropic–mesophase and mesophase–crystalline transitions are observed for the complex, which are consistent with the characters of monotropic LC behavior. The transition peak temperatures and corresponding enthalpy changes of all the complexes are summarized in Table 1.

Table 1. The thermal behavior of complexes[a]

Complex	Heating	Cooling
1/2a	C 133.3[b] I	I 128.7 M 113.7 C
	(69.37)[c]	(–6.81) (–50.38)
1/2b	C 100.8 M 134.0 I	I 123.0 M 92.1 C
	(30.33) (19.30)	(–17.33) (–28.04)
1/2c	C 152.5 M 182.6 I	I 164.4 M 138.6 C
	(46.80) (10.38)	(–4.71) (–46.65)

[a] C: crystal, M: mesophase, I: isotropic. On 1st cooling and 2nd heating. [b] Transition peak temperature in ℃. [c] Transition enthalpy ΔH in J/g.

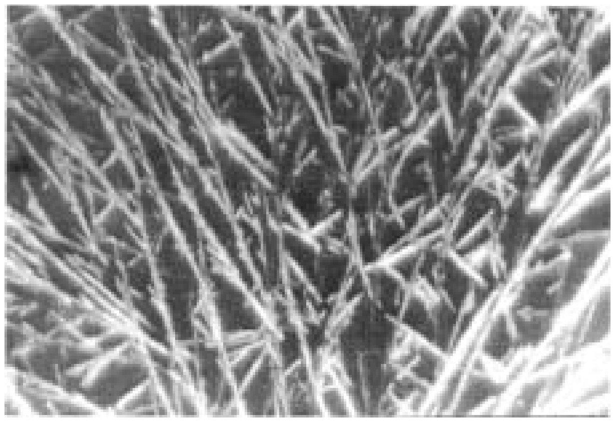

Figure 2. Cross-polarized photomicrograph of the complex **1/2c** at 155 ℃ on cooling (100×).

Under cross-polarized optical microscope, complex **1**/**2a** was observed analogic focal conic texture between 128 °C and 110 °C only on cooling, while complex **1**/**2b** showed a texture similar to that of **1**/**2a** both on heating and on cooling, the temperature intervals coincided with DSC results. These textures were similar to those of 4-alkoxy-4'-stilbazoles[13] and benzoic acid/dipyridyl complexes,[14] which were ascribed to smectic liquid crystals.[13,14] Whereas a dendritic growth texture was observed for the complex **1**/**2c** both on heating and cooling, Figure 2 shows the texture at 155 °C on cooling and it could recover almost completely when the same temperature was reached during heating cycle. Similar dendritic growth texture was ever reported in the monotropic LC phase of hydrogen bonding associated side-chain polyacrylate supramolecular liquid crystals from benzoic acid and bis(acylamino)pyridine components, which was ascribed to columnar phases.[10] The determination of the exact LC types of the complexes herein remains to be confirmed by the temperature varied X-ray diffraction analysis.

We attribute these results mentioned above to the formation of T-shaped supramolecular LC complexes shown in Figure 3. The complexes are built by the doubly hydrogen-bonded self-assembly of the benzoic acid derivatives and 2,6-bis(4-hexyloxybenzoylamino)pyridine.

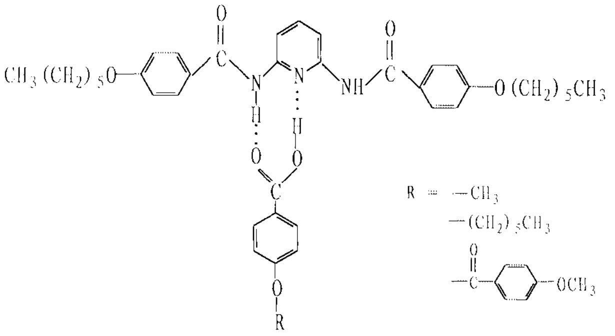

Figure 3. Doubly hydrogen-bonded T-shaped mesogens.

By comparison of the three complexes, it could be concluded that both the introduction of the longer alkoxy(**1**/**2b**) and the extension of the rigid part of the benzoic acid derivatives(**1**/**2c**) have enhanced the thermal stability of the hydrogen-bonded supramolecular liquid crystals and resulted in the transition from the monotropic(**1**/**2a**) to enantiotropic liquid crystals.

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References and Notes

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11 The complexes were prepared by slow evaporation of the 1:1 molar ratio mixtures from 2wt% pyridine solution.
12 Compound **2a** was commercially available from Shanghai Chemical Reagents Company, recrystallized from ethanol, mp 185 °C. Compound **2b** was synthesized according to literature (B. Jones, *J. Chem. Soc.*, **1935**, 1874), which showed nematic liquid crystal between 106.2 °C and 154.8 °C on heating. Elemental analysis (EA) for **2b**: C 70.32% (calc. 70.24), H 8.27% (8.16). Compound **2c** was prepared by a Schotten–Baumann reaction between 4-methoxybenzoyl chloride and 4-hydroxybenzoic acid, and showed nematic liquid crystal between 218.8 °C and 265.7 °C on heating. EA for **2c**: C 65.98% (calc. 66.17), H 4.44% (4.44). The thermal transition temperatures of **2c** are in good agreement with Zhou et al.'s results (Z. Li, Y. Guo, C. Zhang, and Q. F. Zhou, *Acta Polym. Sinica*, **1995**, 414).
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