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Preliminary communication

Miscibility of a hydrogen-bonded mesogenic complex with normal liquid crystals

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Recently, there has been increasing interest in the use of hydrogen bonding between *different* molecular species for building new liquid crystals [1–3]. A variety of low molar mass liquid crystals [4–7], polymeric liquid crystals [8, 9], and mesogenic networks [10] have been built through intermolecular hydrogen bonds. Furthermore, the applicability of hydrogen-bonded liquid crystals for electro-optic devices has been studied for both smectogenic and nematogenic complexes [11–17]. The induction of chiral smectic C phases and ferroelectric properties have also been observed for hydrogen-bonded complexes derived from chiral molecular components [11–14]. Moreover, room-temperature nematic phases can be achieved for complexes of benzoic acid derivatives and simple 4-alkylpyridines [15–17], and alignment on rubbed surfaces and electro-optic effects in a twisted nematic cell have been observed for the room temperature nematics [16].

The applicability of hydrogen-bonded liquid crystals may be widened if these materials can be used in mixtures with normal liquid crystals that are used for display devices. In the present communication, we report liquid crystalline properties for binary mixtures of a hydrogen-bonded mesogenic complex with normal liquid crystal materials which involve only covalent bonds.

We selected a 1:1 complex (**6OBA/8Py**) [15, 16] consisting of 4-hexyloxybenzoic acid and 4-octylpyridine as a hydrogen-bonded mesogenic complex, and 4-octylphenyl 4-hexyloxybenzoate (**OPHOB**) [16, 18] and 4′-heptyl-4-cyanobiphenyl (**7CB**) [19] as normal liquid crystals for miscibility study. The molecular structures of these materials are given in figure 1. Complex **6OBA/8Py** shows a nematic phase from 50 to 31°C on cooling; a nematic phase is seen for 4-hexyloxybenzoic acid (**6OBA**) from 151 to 95°C on cooling, while 4-octylpyridine (**8Py**) is an isotropic liquid at room temperature and exhibits no mesomorphic behaviour. Upon cooling, compound **OPHOB** exhibits isotropic–nematic, nematic–smectic A, and smectic A–crystal transitions at 59, 39, and 11°C, respectively; compound **7CB** displays a nematic phase from 40 to 2°C.

The binary phase diagram for mixtures of **6OBA/8Py** and **OPHOB** is shown in figure 2. The phase transition behaviour was observed visually on cooling. Complex **6OBA/8Py** is miscible with **OPHOB** and no phase separation is observed. The mixtures of these two nematogenic materials exhibit nematic phases over the entire range of composition; the I–N transition temperature behaviour is almost linear.

It is known that in an ideal system the clearing point

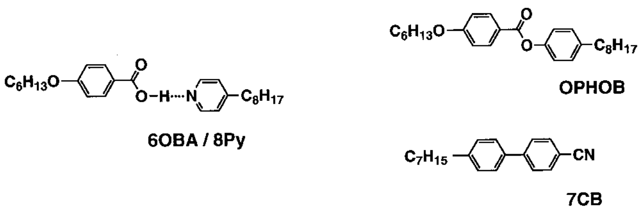

Figure 1. Structures of the hydrogen-bonded liquid crystal complex and normal liquid crystal materials used in this study.

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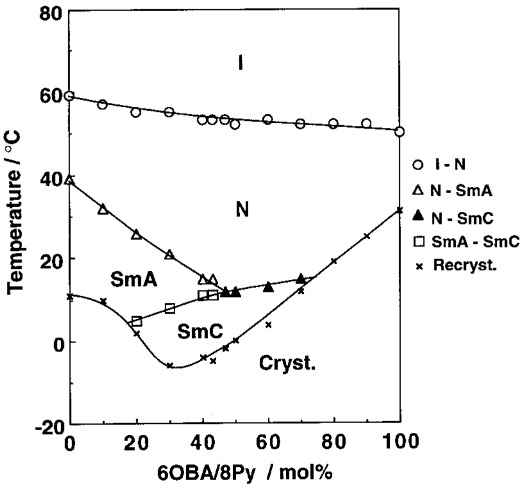

Figure 2. Binary phase diagram for mixtures (mol %) between hydrogen-bonded complex **6OBA/8Py** and normal liquid crystal **OPHOB**.

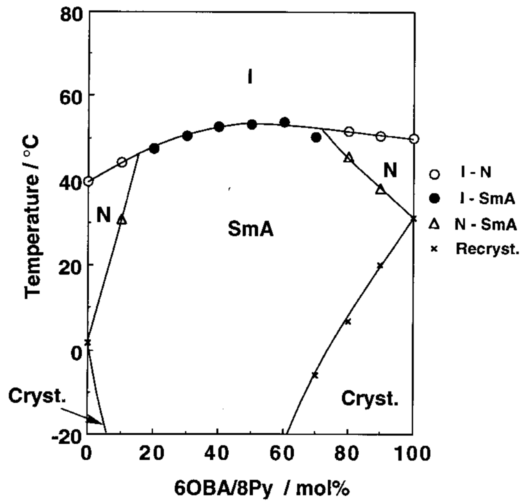

Figure 3. Binary phase diagram for mixtures (mol %) between hydrogen-bonded complex **6OBA/8Py** and normal liquid crystal **7CB**.

(T_c) in mesomorphic mixtures is expressed by equation (1)

$$T_c = \sum_i a_i T_{ci} \tag{1}$$

where a_i is the fraction of component i in the mixture and T_{ci} is its clearing point [20]. The N–I curve in a binary phase diagram is ideally a straight line. The linear trend of the clearing points suggests that no specific interaction exists between **6OBA/8Py** and **OPHOB**. The smectic A phase is observed for mixtures containing less than 45 mol % of **6OBA/8Py**. The smectic C phase is seen between 20 and 70 mol % of **6OBA/8Py**. These results suggest that the hydrogen-bonded mesogenic structure of **6OBA/8Py** is stable in the normal liquid crystal material **OPHOB**.

The phase transition behaviour of mixtures of **7CB** and **6OBA/8Py** is exhibited in figure 3. Complex **6OBA/8Py** is miscible with **7CB**; however this binary phase diagram is quite different from that of **6OBA/8Py** and **OPHOB**. Addition of 10 mol % of **6OBA/8Py** to **7CB** induces a smectic A phase, and only the smectic A phase is observed in the **6OBA/8Py** concentration range between 20 and 70 mol %. Moreover, the curve of the clearing points shows a positive deviation. In some cases, mixing of nematogenic compounds of high and low dielectric anisotropy leads to induction and enhancement of smectic properties [20–24]. Although such induction is inferred for these so-called polar–nonpolar systems, the behaviour of the induced smectic phases cannot be predicted and is empirical [20, 21]. Furthermore, polar–nonpolar systems do not always enhance smectic phases [24]. In the present case, interactions between the cyanobiphenyl and the hydrogen-bonded mesogen with a polar group in the centre of the core structure may affect the molecular ordering and induce the layered structure.

In conclusion mesomorphic behaviour has been examined for binary mixtures of a hydrogen-bonded mesogenic complex (**6OBA/8Py**) consisting of 4-hexyloxybenzoic acid and 4-octylpyridine with normal liquid crystal materials, 4-octylphenyl 4-hexyloxybenzoate (**OPHOB**) and 4′-heptyl-4-cyanobiphenyl (**7CB**). Complex **6OBA/8Py** is miscible with both **OPHOB** and **7CB**. Both nematic and smectic phases are seen for the mixtures of **6OBA/8Py** and **OPHOB** over wide ranges of composition. Induced smectic A phases are dominant in the phase diagram of **6OBA/8Py** and **7CB**, while each of the components is nematogenic.

We have demonstrated that a hydrogen-bonded mesogenic complex is miscible with normal liquid crystal materials. The mixing of hydrogen-bonded and normal liquid crystal materials leads to different types of mesomorphic behaviour.

References

[1] Kato, T., and Fréchet, J. M. J., 1995, *Macromol. Symp.*, **98,** 311.

[2] Kato, T., *Handbook of Liquid Crystals*, edited by D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, and V. Vill. (VCH) (in press).

[3] Kato, T., 1996, *Supramolecular Science*, **3,** 53.

[4] Kato, T., and Fréchet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[5] Kato, T., Fréchet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Fujishima, A., Jin, C., and Kaneuchi, F., 1993, *Chem. Mater.*, **5,** 1094.

[6] Kato, T., Kubota, Y., Nakano, M., and Uryu, T., 1995, *Chem. Lett.*, 1127.

[7] Willis, K., Price, D. J., Adams, H., Ungar, G., and Bruce, D. W., 1995, *J. mater. Chem.*, **5,** 2195.

[8] Kato, T., and Fréchet, J. M. J., 1989, *Macromolecules*, **22,** 3818.

[9] Brandys, F. A., and Bazuin, C. G., 1996, *Chem. Mater.*, **8,** 83.

[10] Kato, T., Kihara, H., Kumar, U., Uryu, T., and Fréchet, J. M. J., 1994, *Angew. Chem., int. Ed. Engl.*, **33,** 1644.

[11] Kumar, U., Fréchet, J. M. J., Kato, T., Ujiie, S., and Iimura, K., 1992, *Angew. Chem., int. Ed. Engl.*, **31,** 1531.

[12] Kato, T., Kihara, H., Uryu, T., Ujiie, S., Iimura, K., Fréchet, J. M. J., and Kumar, U., 1993, *Ferroelectrics*, **148,** 161.

[13] Kihara, H., Kato, T., Uryu, T., Ujiie, S., Kumar, U., Fréchet, J. M. J., Bruce, D. W., and Price, D. J., 1996, *Liq. Cryst.*, **21,** 25.

[14] Yu, L. J., 1993, *Liq. Cryst.*, **14,** 1303.

[15] Fukumasa, M., Kato, T., Uryu, T., and Fréchet, J. M. J., 1993, *Chem. Lett.*, 65.

[16] Kato, T., Fukumasa, M., and Fréchet, J. M. J., 1995, *Chem. Mater.*, **7,** 368.

[17] Machida, S., Urano, T. I., Sano, K., and Kato, T., 1997, *Langmuir*, **13,** 576.

[18] Steinstrasser, R., 1972, *Z. Naturforsch*, **276,** 774; Neubert, M. E., Jirousek, M. R., and Hanlon, C. A., 1986, *Mol. Cryst. Liq. Cryst.*, **133,** 223.

[19] Gray, G. W., Harrison, K. J., and Nash, J. A., 1973, *Electron. Lett.*, **18,** 127. (Compound **7CB** was purchased from Merck Ltd and used as supplied.)

[20] Sage, I., 1987, *Thermotropic Liquid Crystals*, edited by G. W. Gray (Chichester: Wiley).

[21] Chan, L. K. M., Gray, G. W., Lacey, D., Srithanratana, T., and Toyne, K. J., 1987, *Mol. Cryst. Liq. Cryst.*, **150b,** 335.

[22] Engelen, B., Heppke, G., Hopf, R., and Schneider, F., 1978, *Ann. Phys.*, **3,** 403.

[23] Schad, Hp., and Osman, M. A., 1983, *J. chem. Phys.*, **79,** 5710.

[24] Domon, M., and Billard, J., 1979, *J. de Phys.*, **40,** C3–413.