Synthesis and physical properties of α-(4-cyanobiphenyl-4'-yloxy)-ω-[4-(5-alkylpyrimidine-2-yl)phenyloxy]alkanes

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Synthesis and physical properties of α-(4-cyanobiphenyl-4′-yloxy)-ω-[4-(5-alkylpyrimidine-2-yl)phenyloxy]alkanes

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We prepared a homologous series of dimeric liquid crystals, α-(4-cyanobiphenyl-4′-yloxy)-ω-[4-(5-alkylpyrimidine-2-yl)phenyloxy]alkanes (*m*PY*n*OCB), in which cyanobiphenyl and phenylpyrimidine moieties are connected via a flexible central spacer. We investigated the physical properties of *m*PY*n*OCB and of binary mixtures between the dimeric compounds. The interdigitated anticlinic smectic C (SmCanti) phase was found to be induced for some binary mixtures between the dimers with a different odd-numbered spacer. Furthermore, a striped pattern was observed in the SmCanti phase of a homeotropically aligned sample. The striped pattern was propagated when the temperature of the sample was varied. We discuss the correlation between the structure of the SmCanti phase and the appearance of the striped pattern.

1. Introduction

Frustrated phenomena form one of the most exciting areas in liquid crystal science. Since the discovery of the first SmA–SmA transition by Sigaud *et al.* [1], frustrated smectic phases have been observed in pure compounds or in binary mixtures of polar molecules. The dipoles easily form pairs of anti-parallel molecules and the long range organization of the position of the polar heads generates different forms of smectic A phases, i.e. monolayer SmA_1, bilayer SmA_2, partially bilayer SmA_d and the smectic A antiphase which has a transverse modulation of the structure [2–4]. Incommensurate smectic phases, in which SmA_d and either SmA_1 or SmA_2 periodic density waves coexist along the layer normal, have been proposed [5]. Experimental observations of the incommensurate phases have been reported [6–8]. The frustration in these smectic phases results from the competition between periodicity formed by the electrostatic interaction and length of the constituted molecule. On the other hand, chirality is another important factor in the appearance of frustrated phases. Chirality-dependent frustrated phases, i.e. blue phases [9] and the twist grain boundary (TGB) phase [10], have been discovered. Recently the smectic blue phase was

also observed [11, 12]. TGB and smectic blue phases are organized as a result of the competition between twist deformation in smectic phases and the tendency for the molecules to form a layered structure [13]. Furthermore, unusual chirality-dependent phase structures have been observed in some dichiral mesogens as a result of frustration between interlayer and intralayer interactions [14, 15]. The frustrated phases are recognized as liquid crystalline phases with a hierarchical structure.

The design of novel supermolecules is a promising approaches in finding interesting frustrated liquid crystalline phases. Supramolecular assemblies composed of supermolecules, i.e. dimeric and oligomeric liquid crystals, are current topics in the field of liquid crystalline chemistry [16]. Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low-moar-mass mesogens. For example, the transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Many kinds of dimeric and trimeric mesogenic molecules have been reported [17, 18]. Recently, Coles and Pivnenko reported that eutectic mixtures of some fluorosubstituted symmetric liquid crystal dimers doped with a small percentage of a highly twisting chiral additive shows a BPI phase of a very wide temperature range [19]. The introduction of a bent-shape into a molecular structure is another important

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strategy in designing the supermolecules. In 1,3-benzene derivatives first synthesized by Matsunaga *et al.* [20], antiferroelectric and ferroelectric properties have been found by Watanabe *et al.* [21, 22]. The rigid banana-shaped system has provided new concepts for chirality and phase structures in liquid crystals [23, 24]. We have reported novel liquid crystal oligomers, i.e. U-shaped molecule [25], binaphthyl derivatives [26] and a λ-shaped molecule [27] as shown in figure 1. The U-shaped molecule was found to induce unusual ordering in the nematic phase; the binaphthyl derivatives exhibited a blue phase with a wide temperature range and induced a TGB phase in mixtures with the corresponding monomeric compound. Furthermore, the λ-shaped molecule exhibited a stable incommensu-rate SmA phase. Thus, the liquid crystal oligomers were found to induce various frustrated phases in the supramolecular liquid crystalline phase.

We have now prepared dimeric liquid crystals, α-(4-cyanobiphenyl-4′-yloxy)-ω-[4-(5-alkylpyrimidine-2-yl)phenyloxy]alkanes (*m*PY*n*OCB) where cyanobiphe-nyl and phenylpyrimidine moieties are connected via a flexible central spacer [28]. A novel frustrated liquid crystalline phase (Mx phase) was obtained in some binary mixtures between 6PY9OCB and 8PY11OCB, which appeared below a nematic or smectic A phase but was found not to possess a clear layered structure [29].

We report the synthesis of a homologous series of *m*PY*n*OCB compounds and their structure–property relationships. An anticlinic SmC (SmCanti) was found to be induced in some binary mixtures between the polar dimeric compounds. We observed unusual pattern formation and its propagation in a homeotropic sample of the SmCanti phase.

2. Experimental

2.1. *Preparation of 1-(4-cyanobiphenyl-4′-yloxy)-7-[4-(5-dodecylpyrimidine-2-yl)phenyloxy]heptane, 12PY7OCB*

5-Alkyl-2-(4-hydroxyphenyl)pyrimidine was obtained from Midori Chemical Corporation. The synthetic route for a typical compound is shown in scheme 1. To a solution of 4-cyano-4′-hydroxybiphenyl (1.18 g,
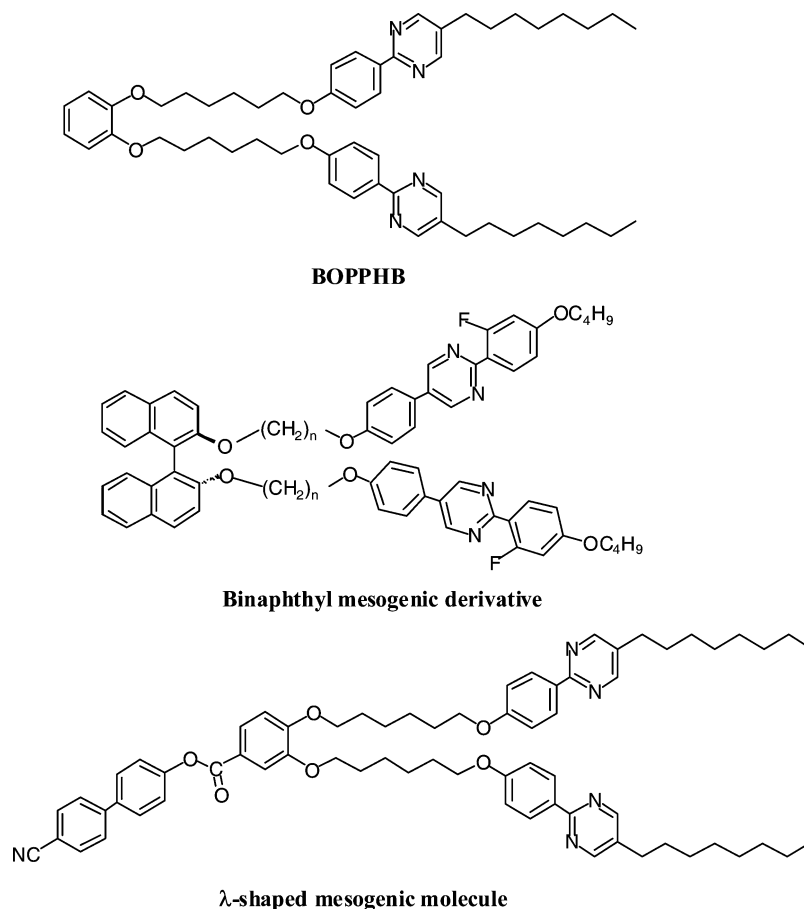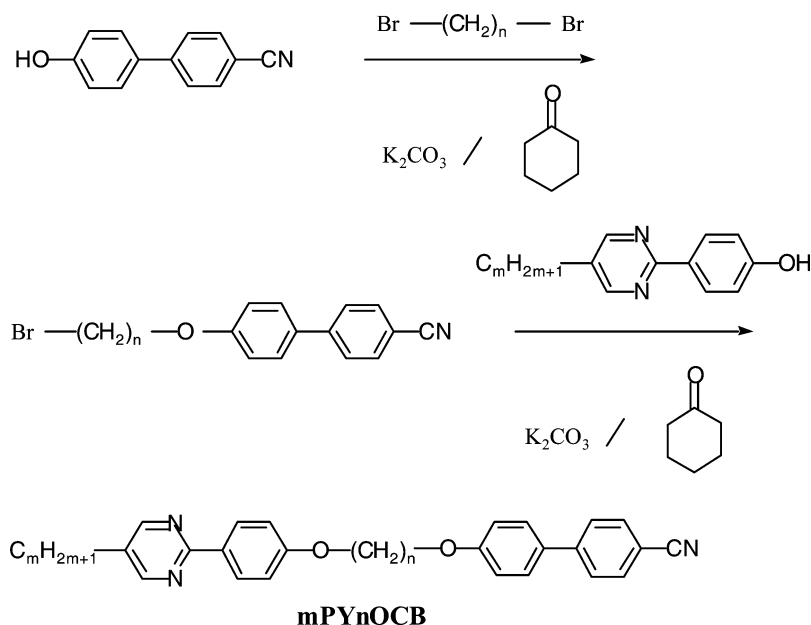

BOPPHB

Binaphthyl mesogenic derivative

λ-shaped mesogenic molecule

Figure 1.   Liquid crystal oligomers with unusual liquid crystalline phases.

Scheme 1. Synthetic route for *m*PY*n*OCB compounds.

6.1 mmol) and 1,7-dibromohexane (2.35 g, 9.1 mmol) in cyclohexanone (15 ml) was added potassium carbonate (0.83 g, 6.0 mmol); the reaction mixture was stirred at 80°C for 4 h. After filtration of the precipate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane/hexane (3/2) mixture as eluant. 4-Cyano-4′-(7-bromoheptyloxy)biphenyl was obtained; yield 1.28 g (3.4 mmol, 57%).

To a solution of 4-cyano-4′-(7-bromoheptyloxy)biphenyl (1.28 g, 3.4 mmol) and 5-dodecyl-2-(4-hydroxyphenyl)pyrimidine (1.22 g, 3.6 mmol) in cyclohexanone (13 ml) was added potassium carbonate (0.47 g, 3.6 mmol); the reaction mixture was stirred at 120°C for 5 h. After filtration of the precipate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane/ethylacetate (39/1) mixtute as eluant. Recrystallization from ethanol gave the desired product; yield 1.90 g (3.0 mmol, 88%).

The purity of the final compound was checked by normal phase HPLC (Intersil SIL 150A-5 column). A dichloromethane/isopropylalcohol (85/15) mixture was used as eluant. Detection of the products was achieved by UV irradiation (λ=254 nm). The structure of the final product was elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270). ^{1}H(270 MHz, solvent CDCl$_3$, standard TMS): δ_H/ppm: 8.56(s, 2H, Ar–**H**), 8.35(d, 2H, Ar–**H**, J=8.9 Hz), 7.69–7.60(m, 4H, Ar–**H**), 7.51(d, 2H, Ar–**H**,

J=8.9 Hz), 6.98(d, 2H, Ar–**H**, J=8.9 Hz), 6.97(d, 2H, Ar–**H**, J=9.2 Hz), 4.03(t, H, –O**CH**$_2$–, J=6.5 Hz), 4.01(t, 2H, –O**CH**$_2$–, J=6.2 Hz), 2.59(t, 2H, J=7.6 Hz), 1.88–1.78(m, 4H, aliphatic–**H**), 1.66–1.21(m, 26H, aliphatic–**H**), 0.88(t, 3H, –**CH**$_3$, J=6.8 Hz). IR (KBr) v_{max}/cm^{-1}: 2922, 2850, 2234, 1606, 1582, 1496. Purity: 100%.

The other compounds reported here were prepared by a similar method to that for compound 12PY7OCB.

2.2. *Liquid crystalline and physical properties*

The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5°C min^{-1}, unless otherwise indicated. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The compounds were studied at a scanning rate of 5°C min^{-1}, for both heating and cooling cycles, after encapsulation in aluminum pans. A homeotropically aligned cell with the inner surfaces coated with cetyltrimethylanmonium bromide was purchased from E. H. C. Co., Ltd. The cell gap was 5±0.5 μm. The X-ray scattering experiments were performed using a real-time X-ray diffractometer (Bruker AXS D8 Discover). The monochromatic X-ray beam (Cu-K$_\alpha$ line) was generated by a 1.6 kW X-ray tube and Göbel mirror optics. The 2D position-sensitive detector has

1024 × 1024 pixels in a $5 \times 5\,cm^2$ beryllium window. A sample was introduced into a thin glass capillary tube (diameter 1.0 mm), which was placed in a custom-made temperature-stabilized holder (stability within $\pm 0.1^{\circ}C$). The X-ray diffraction (XRD) measurements and the textural observations by polarizing optical microscopy (POM) using a CCD camera were performed simultaneously on the sample in the glass capillary tube.

3. Results and discussion

3.1. *Physical properties of mPYnOCB*

Temperatures and enthalpies of transition for *m*PY*n*OCB compounds are compared in table 1. 8PY6OCB, 8PY7OCB, 8PY8OCB and 8PY9OCB, in which the length of the spacer is comparable to that of the terminal chain, showed only a nematic phase. The other compounds exhibited a smectic A phase. 6PY11OCB and 8PY11OCB were found to show an unusual phase sequence of I–N–SmA–SmCanti. Only a few compounds have so far been reported to show the nematic phase and anticlinic SmC phase [28, 30, 31]. A layer spacing of *m*PY*n*OCB in the SmA phase obtained by XRD measurements, and its molecular length estimated by MM2 modelling, are shown in table 2. For non-symmetric dimeric liquid crystals it has been found that two different modifications can exist, depending on the lengths of the spacer and the terminal alkyl chain [17]. For dimers possessing alkyl groups and shorter spacers, an 'interdigitated' SmA (SmAd) phase

Table 1. Temperatures ($^{\circ}$C) and enthalpy changes (kJ mol^{-1}) of transition in parentheses for *m*PY*n*OCB compounds. Square brackets indicate a monotropic transition.

mPYnOCB

Compound	cryst	SmCanti	SmA	N	I	m.p.
6PY9OCB	• 77		[• 83 (0.3)]	• 136 (2.2)	•	112
6PY11OCB	• 77	[• 81[a]]	• 115 (1.6)	• 131 (5.9)	•	103
8PY6OCB	• 123			• 173 (7.0)	•	128
8PY7OCB	• 86			• 129 (1.8)	•	115
8PY8OCB	• 119			• 158 (7.1)	•	127
8PY9OCB	• 80			• 130 (2.2)	•	108
8PY10OCB	• 116		• 141 (2.3)	• 145 (7.4)	•	127
8PY11OCB	• 78	[• 92[a]]	• 115 (1.6)	• 128 (2.9)	•	103
11PY7OCB	• 93		[• 112[a]]	• 124 (1.2)	•	123
12PY5OCB	• 103		[• 124 (6.1)]		•	128
12PY6OCB	• 122		• 166 (8.6)		•	127
12PY7OCB	• 92		[• 116 (0.7)]	• 121 (2.1)	•	120
12PY8OCB	• 120		• 147 (7.5)		•	128
12PY9OCB	• 87		[• 102[a]]	• 122 (2.1)	•	113

[a]Enthalpies too small to be measured.

Table 2. Layer spacing of *m*PY*n*OCB compounds in the SmA phase obtained by X-ray measurements, molecular lengths estimated by MM2 model, and the phase structures, i.e. intercalated smectic A (SmAc) phase or interdigitated smectic A (SmAd).
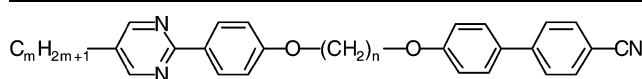
Compound	Layer spacing/ Å	Molecular length/ Å	Phase structure
6PY9OCB	19	36	SmAc
6PY11OCB	20	39	SmAc
8PY11OCB	23	42	SmAc
12PY7OCB	61	42	SmAd
12PY9OCB	67	45	SmAd

was found with a smectic layer spacing (d) of >1.5 times longer than the length (l) of the molecule. When the spacer is longer than the terminal alkyl groups an 'intercalated' SmA (SmAc) phase is observed with a d/l ratio of about 0.5.

3.2. *Phase transition behaviour and physical properties of binary mixtures between mPYnOCBs*

We have already noted that a novel mesophase denoted as Mx phase appears below a N or SmA phase of some binary mixtures between 6PY9OCB and 8PY11OCB. Both of these compounds have a SmAc phase. We investigated the transition behaviour of a binary mixture between 12PY7OCB and 12PY9OCB. Both compounds have the interdigitated SmA (SmAd) phase. Figure 2 shows the binary phase diagram on cooling between 12PY7OCB and 12PY9OCB; the N and SmAd phases of both compounds proved to be miscible across the full composition range. The Mx phase was not observed. However, a SmCanti phase was found to
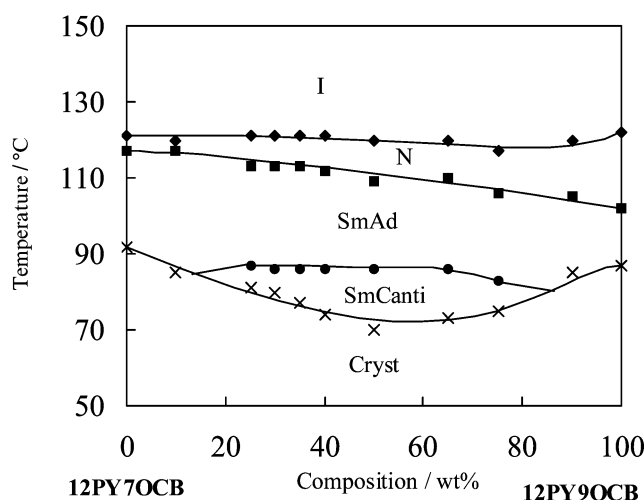

Figure 2. Phase diagram for mixtures of 12PY7OCB and 12PY9OCB.

be induced for mixtures containing 25–75 wt% of 12PY9OCB. The SmCanti phase was identified by optical microscopy, i.e. the texture of the homeotropically aligned sample showed a schlieren texture which possessed singularities with both two ($s=1/2$) and four ($s=1/4$) brushes [32]. A texture of the sample in the SmA phase was completely dark under POM, thus, we assumed that the layer normals of the SmA and SmCanti phases are perpendicular to the glass plate.

We investigated physical properties of a 50/50 wt% mixture of 12PY7OCB and 12PY9OCB. Transition temperatures and enthalpies of transition of the mixture were I 120°C ($2.9\,J\,g^{-1}$) N 109°C ($0.05\,J\,g^{-1}$) SmA 86°C ($0.2\,J\,g^{-1}$) SmCanti 70°C recryst. The melting temperature was 107°C, and the SmCanti phase was monotropic. An explanation of the appearance of a SmCanti phase could be that these mixtures may be supercooled sufficiently to reveal the phase. The enthalpy of the N to SmA transition was very small. XRD measurements were performed for the mixture; patterns for the mixture in the SmA and SmCanti phases are shown in figure 3. A layer spacing of about 65 Å was obtained both in the SmA and SmCanti phases, which is the average of the layer spacings of 12PY7OCB and 12PY9OCB in the interdigitated SmA phase. Thus, the SmA and SmCanti phases of the mixture are also considered to exhibit 'interdigitated' smectic phases. The layer spacing did not change from the SmA phase to the SmCanti phase.

We investigated the effect of spacer and terminal chain lengths of *m*PY*n*OCB on the phase transition behaviour of binary mixtures. Figure 4 shows a phase 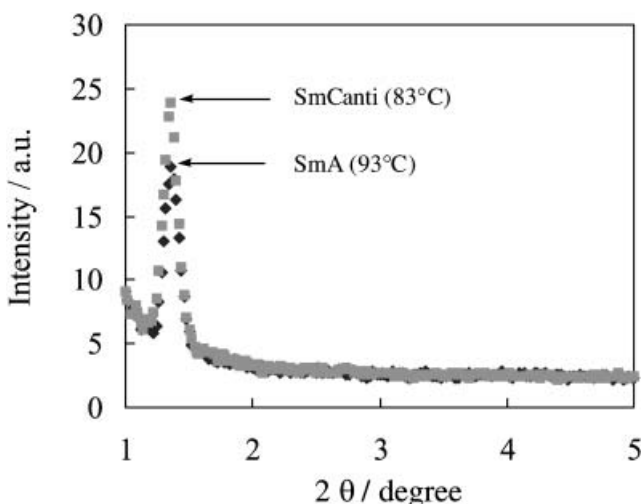diagram on cooling between 6PY11OCB and 8PY11OCB. The N, SmAc, and SmCanti phases of both materials proved to be miscible across the full composition range. The Mx phase was not induced in the binary phase diagram. The difference in the spacer length between the dimeric compounds is one reason for the appearance of the Mx phase. A layer spacing of 20.5 Å was obtained at 80°C in the SmCanti phase of 6PY11OCB, indicating that the SmCanti phase has an intercalated structure. Although we did not measure a layer spacing in the SmCanti phase of 8PY11OCB, the miscibility between both the SmCanti phases suggests that the SmCanti phase of 8PY11OCB also has an intercalated structure.

Figure 5 (*a*) shows a binary phase diagram on cooling between 8PY11OCB and 12PY7OCB. Both compounds exhibit the same molecular length on the basis of MM2 calculation, whereas they have different SmA phase structures; i.e. an intercalated SmA phase for 8PY11OCB and an interdigitated SmA phase for 12PY7OCB. The N phase of the two compounds proved to be miscible across the full composition range. The intercalated SmA phase of 8PY11OCB was not miscible with the interdigitated SmA phase of 12PY7OCB. The SmCanti phase was found to be induced for mixtures containing 35–70 wt% of 12PY7OCB. Furthermore the Mx phase appeared in the mixture containing 50 wt% of 12PY7OCB. The Mx phase appeared in a very narrow temperature range; however, its characteristic texture was clearly detected by optical microscopy. The melting temperature of the mixture was 106°C, so the Mx and SmCanti phases are monotropic liquid crystalline phases. XRD measurements were performed for the mixture; a spacing of 65 Å for a sharp peak at $2\theta=1.35$ was obtained, indicating that the SmCanti phase has an interdigitated structure.
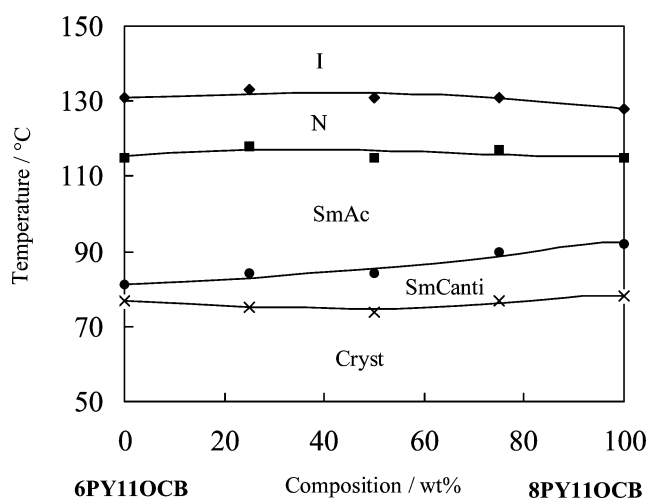

Figure 3. XRD patterns for the 50/50 wt% mixture of 12PY7OCB and 12PY9OCB in the SmA at 93°C and SmCanti phases at 83°C.

Figure 4. Phase diagram for mixtures of 6PY11OCB and 8PY11OCB.

become related to one another, see figure 6 (*b*). Both the SmA and SmCanti phases are considered to have an interdigitated structure. The interdigitated SmCanti phase, composed of dimeric compounds of different molecular lengths, is thought to have unfavourable free volume or unfavourable density distribution. The interdigitated SmCanti phase may have a larger free volume than the intercalated SmCanti phases of 6PY11OCB, 8PY11OCB, or of binary mixtures between them (see figure 4). Watanabe *et al.* reported an antiferroelectric smectic liquid crystal formed by an achiral twin dimer with two identical mesogenic groups connected by an odd-membered spacer [33]. The spacer length is much shorter than the terminal alkyl chains. The layer spacing is approximately equal to the length of the molecules in the bent conformation. They proposed possible smectic structures with bilayer modification formed by dimers when the alkyl tail and spacer segregate from each other. The SmCanti phase induced in the mixtures was only observed for binary mixtures with an odd-membered spacer, and was found to be an interdigitated structure. If the constituent molecules have a bent structure and the dipoles can form pairs of anti-parallel molecules in the interdigitated
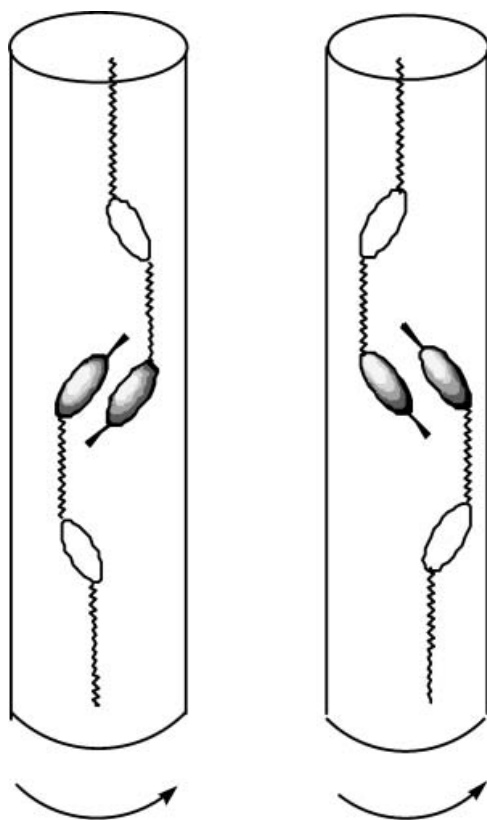
structure, there might be three alternating tilting parts in each layer as shown in figure 6 (*b*). The assumption that the dimers exist only in extended conformations is not sufficient when discussing the structure–property relationships. They may exist also in horseshoe-like conformations [17]. Recently, Luckhurst *et al.* reported that experiments on the dielectric relaxation in symmetric and non-symmetric dimers have been successfully explained in terms of a temperature-dependent equilibrium between extended and bent conformations [34]. However, the SmCanti phase present in the mixtures is only found for binary mixtures composed of odd-spaced compounds.

3.4. *Pattern formation*

The homeotropically aligned samples of the SmCanti phase induced in some mixtures between 12PY7OCB and 12PY9OCB showed a quite unique striped pattern, see figure 8. When the sample was rotated clockwise about 45°, the dark stripes barely changed to be bright. This observation indicates that the black region is almost an optically uniaxial state.

The striped pattern was propagated when the temperature of the sample was varied. Pattern propagation was observed through the whole temperature range of the SmCanti phase, i.e. from a temperature just below the SmA–SmCanti transition until crystallization. The propagation speed depended on the cooling or heating rate, i.e. on increasing the cooling or heating rate, the propagation speed increased. Figure 9 shows photomicrographs of the striped pattern of a 50/50 wt% mixture of 12PY7OCB and 12PY9OCB contained in a homeotropically aligned cell, cell gap 5 μm, on cooling under crossed polarizers. The width of the stripes differed among different domains; however, those in the same region of the homeotropic sample did not

Figure 8. Photomicrograph of the homeotropically aligned SmCanti phase at 80°C formed by a 50/50 wt% mixture of 12PY7OCB and 12PY9OCB. Magnification × 50.

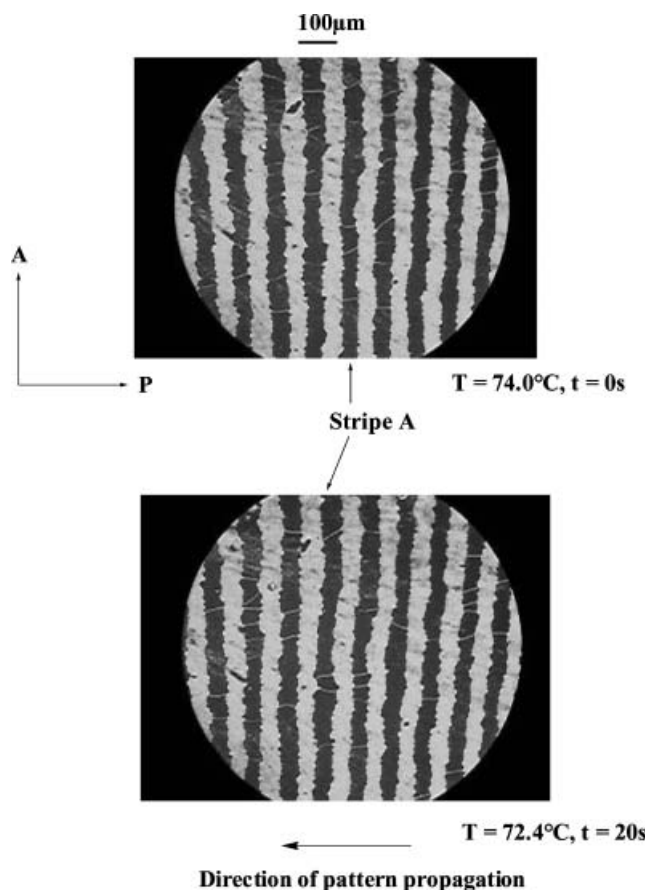Figure 7. A possible model for the interdigitated SmA phase of a mixture.

100μm

Figure 9. Photomicrographs of the striped pattern of a mixture of a 50/50 wt% 12PY7OCB and 12PY9OCB contained in a homeotropically aligned cell, cell gap 5 μm, on cooling under crossed polarizers. Cooling rate 5°C min^{-1}.

change markedly as a function of temperature (see figure 9). The pattern formation and its propagation were observed for other induced interdigitated SmCanti phases of some binary mixtures between homologues with different odd-membered spacer, e.g. 11PY7OCB– 12PY9OCB, 12PY5OCB–12PY7OCB, 12PY5OCB– 12PY9OCB, 8PY11OCB–12PY7OCB, and 8PY11OCB –12PY9OCB. On the other hand, they were not observed in the intercalated SmCanti phases of 6PY11OCB, 8PY11OCB, and mixtures between them.

Pattern formation in liquid crystals is one of the central problems in liquid crystal science [35, 36]. Dissipative structures have been observed in some nematic liquid crystalline systems under electric or magnetic fields [37, 38]. Front propagation in smectic liquid crystals has been investigated [39–46]. Recently, Stannarius and Weissflog observed propagating waves with sharp fronts at a phase transition in liquid crystalline freestanding films of an achiral hockey stick-shaped mesogen [47]. They interpreted this

phenomenon as synclinic to anticlinic transitions of individual smectic layers or stacks of layers. Textures which are somewhat similar to the striped pattern have been observed in a biaxial SmA phase of a binary system between a metallomesogen and 2, 4, 7-trinitro-fluorenone [48], and also in that of a bent-core molecule [49]. However, a striped texture, consisting of alter-nately aligned dark and bright domains, was obtained in the mixture studied here. We cannot give a clear explanation for the pattern formation in the SmCanti phase. Although a helical arrangement can produce a striped texture, we have no experimental proof for the existence of a helical structure in the SmCanti phase from microscopic observation. The mechanism of pattern formation is now being investigated.

4. Conclusions

We prepared a homologous series of dimeric liquid crystals, α-(4-cyanobiphenyloxy)-ω-[4-(5-alkylpyrimi-dine-2-yl)phenyloxy]alkanes (*m*PY*n*OCB) where cyano-biphenyl and phenylpyrimidine moieties are connected via a flexible central spacer. The interdigitated SmCanti phase was found to be induced for some binary mixtures between the bimesogenic compounds with differing odd-membered spacers. At least one of them has an interdigitated SmA phase. Furthermore, we observed a striped pattern formation in the induced interdigitated SmCanti phase of a homeotropically aligned sample, and observed pattern propagation when the temperature of the sample was varied. Coupling between polar groups and the bent structure produces the frustrated phenomena.

References

[1] G. Sigaud, F. Hardouin, M.F. Achard. *Phys. Lett.*, **72A**, 24 (1979).
[2] A.M. Levelut, R.J. Tarento, F. Hardouin, M.F. Achard, G. Sigaud. *Phys. Rev. A*, **24**, 2180 (1981).
[3] V. Faye, H.-T. Nguyen, P. Barois. *J. Phys. II Fr.*, **7**, 1245 (1997).
[4] P. Barois. In *Handbook of Liquid Crystals*, Vol. 1, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 281–309, Wiley-VCH, Weinheim (1998).
[5] J. Prost, P. Barois. *J. chim. Phys. phys.-chim. Biol.*, **80**, 65 (1983).

[6] J.T. Mang, B. Cull, Y.S. Shi, P. Patel, S. Kumar. *Phys. Rev. Lett.*, **74**, 4241 (1995).

[7] (*a*) F. Hardouin, M.F. Achard, J.L. Jin, J.W. Shin, Y.K. Yun. *J. Phys. II Fr.*, **4**, 627 (1994); (*b*) F. Hardouin, M.F. Achard, J.L. Jin, Y.K. Yun. *J. Phys. II Fr.*, **5**, 927 (1995).

[8] J.M. Seddon. In *Handbook of Liquid Crystals*, Vol. 1, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 635–679, Wiley-VCH, Weinheim (1998).

[9] P.P. Crooker. *Liq. Cryst.*, **5**, 751 (1989).

[10] (*a*) J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, J.S. Patel. *J. Am. chem. Soc.*, **111**, 8119 (1989); (*b*) J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, J.S. Patel. *Nature*, **337**, 449 (1989).

[11] E. Demikhov, H. Stegemeyer. *Liq. Cryst.*, **10**, 869 (1991).

[12] (*a*) M.-H. Li, V. Laux, H.-T. Nguyen, G. Sigaud, P. Barois, N. Isaert. *Liq. Cryst.*, **23**, 389 (1997); (*b*) B. Pansu, M.H. Li, H.-T. Nguyen. *J. Phys. II Fr.*, **7**, 751 (1997).

[13] J.W. Goodby. In *Handbook of Liquid Crystals*, Vol. 1, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 115–132, Wiley-VCH, Weinheim (1998).

[14] (*a*) A. Yoshizawa, J. Umezawa, N. Ise, R. Sato, Y. Soeda, T. Kusumoto, K. Sato, T. Hiyama, Y. Takanishi, H. Takezoe. *Jpn. J. appl. Phys.*, **37**, L942 (1998); (*b*) Y. Takanishi, T. Ogasawara, A. Yoshizawa, J. Umezawa, T. Kusumoto, T. Hiyama, K. Ishikawa, H. Takezoe. *J. mater. Chem.*, **12**, 1325 (2002).

[15] I. Nishiyama, J. Yamamoto, J.W. Goodby, H. Yokoyama. *J. mater. Chem.*, **12**, 1709 (2002).

[16] (*a*) J.W. Goodby, G.H. Mehl, I.M. Saez, R.P. Tuffin, G. Mackenzie, R. Auzely-Velty, T. Benvegnu, D. Plusquellec. *Chem. Commun.*, 2057 (1998); (*b*) I. Saez, J.W. Goodby. *J. mater. Chem.*, 2005, 26 (2005).

[17] C.T. Imrie, G.R. Luckhurst. In *Handbook of Liquid Crystals*, Vol. 1, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 801–833, Wiley-VCH, Weinheim (1998).

[18] C.T. Imrie, P.A. Henderson. *Curr. Opin. colloid interface Sci.*, **7**, 298 (2002).

[19] H.J. Coles, M.N. Pivnenko. *Nature*, **436**, 997 (2005).

[20] T. Akutagawa, Y. Matsunaga, K. Yasuhara. *Liq. Cryst.*, **17**, 659 (1994).

[21] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. mater. Chem.*, **6**, 1231 (1996).

[22] E. Grecka, D. Pociecha, F. Araoka, D.R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe. *Phys. Rev. E*, **62**, R4524 (2000).

[23] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Korblova, D.M. Walba. *Science*, **278**, 1924 (1997).

[24] G. Pelzl, S. Diele, W. Weissflog. *Adv. Mater.*, **11**, 707 (1999).

[25] A. Yoshizawa, A. Yamaguchi. *Chem. Commun.*, 2060 (2002).

[26] (*a*) J. Rokunohe, A. Yoshizawa. *J. mater. Chem.*, **15**, 275 (2005); (*b*) J. Rokunohe, A. Yamaguchi, A. Yoshizawa. *Liq. Cryst.*, **32**, 207 (2005).

[27] A. Yamaguchi, I. Nishiyama, J. Yamamoto, H. Yokoyama, A. Yoshizawa. *J. mater. Chem.*, **15**, 280 (2005).

[28] A. Yoshizawa, N. Ise, T. Okada. *Ferroelectrics*, **214**, 75 (1998).

[29] A. Yoshizawa, K. Yamamoto, H. Dewa, I. Nishiyama, H. Yokoyama. *J. mater. Chem.*, **13**, 172 (2003).

[30] Y. Aoki, H. Nohira. *Liq. Cryst.*, **26**, 97 (1999).

[31] I. Nishiyama, J. Yamamoto, J.W. Goodby, H. Yokoyama. *Liq. Cryst.*, **29**, 1409 (2002).

[32] (*a*) Y. Takanishi, H. Takezoe, A. Fukuda, J. Watanabe. *Phys Rev. B*, **45**, 7684 (1992); (*b*) Y. Takanishi, H. Takezoe, A. Fukuda, H. Komura, J. Watanabe. *J. mater. Chem.*, **2**, 71 (1992).

[33] J. Watanabe, T. Niori, S.-W. Choi, Y. Takanishi, H. Takezoe. *Jpn. J. appl. Phys.*, **37**, L401 (1998).

[34] M. Stocchero, A. Ferrarini, G.J. Moro, D.A. Dunmur, G.R. Luckhurst. *J. chem. Phys.*, **121**, 8079 (2004).

[35] A. Buka, L. Kramer (Eds). *Pattern Formation in Liquid Crystals*, Springer (1996).

[36] Y. Hidaka, S. Kai. *Ekisho*, **4**, 219 (2000).

[37] E. Dbois-Violette, P.G. de Gennes, D. Parodi. *J. Physique.*, **32**, 305 (1971).

[38] S. Kai, K. Hirakawa. *Solid. state. Commun.*, **18**, 1573 (1976).

[39] H. Miike, T. Kohno, K. Koga, Y. Ebina. *J. phys. Soc. Jpn.*, **43**, 727 (1977).

[40] S. Nasuno, N. Yoshimo, S. Kai. *Phys. Rev. E*, **51**, 1598 (1995).

[41] S.T. Largerwall, B. Stebler. *J. Phys. (Paris) C3*, **40**, 53 (1979).

[42] S.T. Largerwall, B. Stebler. In *Ordering in Strongly Fluctuating Condensed Matter Systems*, T. Riste (Ed.), pp. 383–397, Plenum, New York (1980).

[43] N.A. Clark. *Phys. Rev. Lett.*, **40**, 1663 (1978).

[44] P.E. Cladis, H.R. Brand, P.L. Finn. *Phys. Rev. A*, **28**, 512 (1983).

[45] J.E. Maclennan, M.A. Handschy, N.A. Clark. *Phys. Rev. A*, **34**, 3554 (1986).

[46] W. van Saarloos. *Phys. Rev. Lett.*, **58**, 2571 (1987).

[47] R. Stannarius, J. Li, W. Weissflog. *Phys. Rev. Lett.*, **90**, 025502 (2003).

[48] T. Hegmann, J. Kain, S. Diele, G. Pelzl, C. Tschierske. *Angew. Chem. int. Ed.*, **40**, 887 (2001).

[49] B.K. Sadashiva, R. Amaranatha Reddy, R. Pratibha, N.V. Madhusudana. *J. mater. Chem.*, **12**, 943 (2002).