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Self-Assembly of Amphiphilic Liquid-Crystalline Oligomers Possessing a Semiperfluorinated Alkyl Chain

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Amphiphilic liquid-crystalline oligomers composed of a semiperfluorinated alkyl chain and cyanobiphenyl mesogenic moieties were prepared. Their physical properties were investigated using optical microscopy, differential scanning calorimetry, and X-ray diffraction measurements. The oligomers were found to show an unusual phase sequence of lamellar−columnar−bicontinuous cubic phases when the number of cyabobiphenyl moieties was increased. Results of the XRD study suggest that the smectic A phase of the oligomer with a SmA to Cub phase transition has an undulated layer structure. We discuss effects of the molecular structure on the appearance of the columnar and cubic phases of the novel liquid crystal oligomers.

Introduction

Supermolecular assemblies with well-defined morphologies (e.g., layers, interpenetrating networks, columns, and spheroids) are fundamental components for structure formation in biological systems, as well as for application to production of novel functional materials. For those reasons, investigation of the driving forces of this self-assembly process is an important contemporary research topic.[1,2] In particular, cubic liquid-crystalline phases, which represent three-dimensional ordered supramolecular arrangements such as interpenetrating networks and spheroids, have recently attracted much attention.[3,4] Cubic mesophases are common in lyotropic systems, such as surfactant−solvent systems. The mesophase morphologies of these amphiphilic systems are governed mainly by the volume fraction of the two incompatible segments combined in such molecules. The phase sequence of lamellar (smectic, SmA), bicontinuous cubic ($\mathrm{Cub_V}$), hexagonal columnar ($\mathrm{Col_h}$), micellar cubic ($\mathrm{Cub_I}$) upon the volume fraction of one component being increased is typical for morphologies of mesophases of these systems (see Figure 1). The value of the interface curvature between hydrophilic regions and lipophilic regions is recognized as the key factor determining the mesophase morphology of these systems.[1,5] Cubic structures can also be found in amphiphilic block copolymers[6] and polyelectrolytes.[7] In contrast to lyotropic cubic systems, few thermotropic compounds with cubic phase are known. They have been found for nitro-substituted and cyano-substituted biphenyl carboxylic acids,[8,9] dibenzoylhydrazides,[10] polycatenar compounds,[11,12] metal complexes,[13] amphiphilic polyhydroxy compounds,[14,15] and carbohydrate derivatives.[16] In most cases, bicontinuous cubic mesophases have been found for these cubic phases.

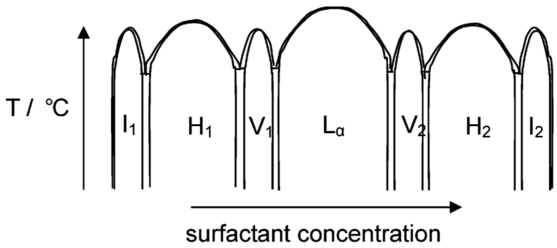

Figure 1. Lyotropic liquid-crystalline phases of a surfactant−solvent system depending on the solvent concentration. I represents a micellar cubic phase, H a hexagonal phase, V a bicontinuous cubic phase, and L a lamellar phase. Subscripts 1 and 2, respectively, indicate normal phases and inverted phases.

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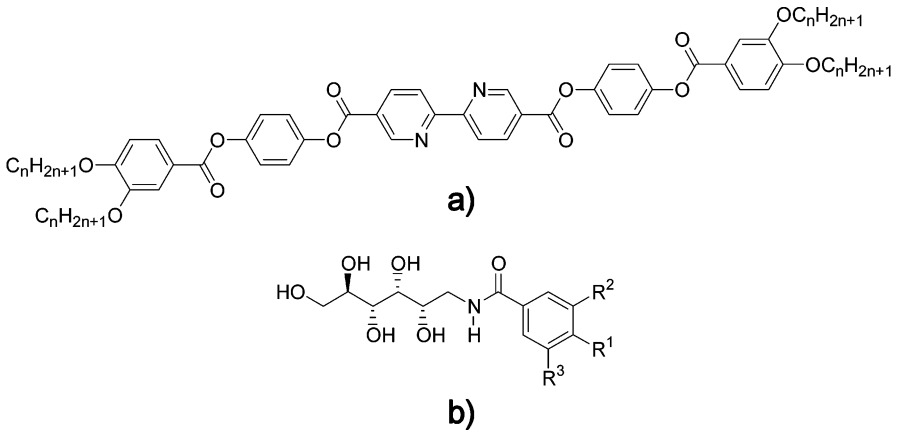

Figure 2. Chemical structures of liquid-crystalline compounds with thermotropic cubic phases: (a) tetracatenar molecule and (b) polyhydroxy derivatives.

In tetracatenar mesogens, like those shown in Figure 2a, which comprise an extended, rigid core and four terminal chains, the phase sequence of SmC−Cub_V−Col is apparent as terminal chains increase. This phase sequence is explained in terms of the curvature in the interface between the aromatic core and the terminal chains and the formation of aggregates of molecules.[12e,13f] In the case of polyhydroxy derivatives, as shown in Figure 2b, the same sequence as that reported for lyotropic systems, SmA−Cub_V−Col_h−Cub_I, was obtained. The mesophase morphologies are dominated by the interface curvature between hydrophilic regions and lipophilic regions.[2c,d]

Preorganization,[17] or a bottom-up approach, is an important concept in the design of mesogenic molecules.[2a−b,18,19] We have reported novel preorganized systems, e.g., U-shaped molecules,[20] binaphthyl derivatives,[21] and λ-shaped molecules;[22] the preorganized compounds were found to induce unusual ordering in the supramolecular liquid-crystalline phase. A λ-shaped molecule, 4-(5-octylpyrimidin-2-yl)-phenyl-3,4-bis{6-[4-(5-octylpyrimidin-2-yl)phenyoxy]-hexyloxy}benzoate, showed a liquid-crystalline phase in which the layer ordering and the deformation of the *n*-director coexist.[22] Such layer deformation of the λ-shaped molecule is expected to engender the formation of columnar and cubic mesophases. Figure 3 shows the designed and prepared amphiphilic liquid-crystalline oligomers that comprise cyanobiphenyl mesogenic moieties and a semiperfluorinated alkyl chain. We found that the introduction of amphiphilic properties into the oligomeric molecules can realize a novel type of a lamellar-to-cubic transition.

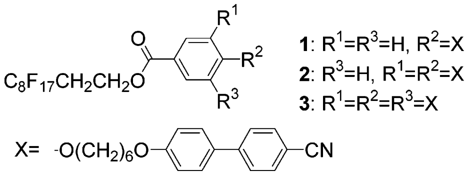

Figure 3. Molecular structures of the amphiphilic oligomers.

Experimental Section

Preparation of Materials. Purification of final products was carried out using column chromatography over silica gel (63−210 μm; Kanto Chemical Co. Inc.) using dichloromethane or a dichloromethane-ethyl acetate mixture as the eluent, followed by reprecipitation with chloroform−methanol. The purities of all final compounds were checked using elemental analysis (EA. 1110; CE Instruments Ltd.). The structures of the final products were elucidated using infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories, Inc.) and proton nuclear magnetic resonance (1H NMR) spectroscopy (JNM-A400; JEOL).

4′-(6-Bromohexyloxy)biphenyl-4-carbonitrile. 4-Cyano-4′-hydroxybiphenyl (1.56 g, 8 mmol) and 1, 6-dibromohexane (3.86 g, 12 mmol) were dissolved in cyclohexanone (20 mL). Potassium carbonate (1.66 g, 12 mmol) was added, and the resulting mixture was stirred at 70 °C for 5 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel (using dichloromethane as eluent). Recrystallization from hexane gave the desired product, yielding 2.04 g (71%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J = 8.4$ Hz, 2H, Ar−H), 7.63 (d, $J = 8.9$ Hz, 2H, Ar−H), 7.52 (d, $J = 8.6$ Hz, 2H, Ar−H), 6.99 (d, $J = 8.6$ Hz, 2H, Ar−H), 4.02 (t, $J = 6.3$ Hz, 2H, OCH_2), 3.43 (t, $J = 6.8$ Hz, 2H, $BrCH_2$), 1.93−1.78 (m, 4H, CH_2), 1.56−

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1.50 (m, 4H, CH_2). IR (KBr): 2942, 2856, 2223, 1602, 1494, 1249, 823 cm^{-1}.

Ethyl 4-[6-(4′-Cyanobiphenyl-4-yloxy)hexyloxy]benzoate. 4′-(6-Bromohexyloxy)biphenyl-4-carbonitrile (0.72 g, 2 mmol) and ethyl 4-hydroxybenzoate (0.33 g, 2 mmol) were dissolved in cyclohexanone (3 mL). K_2CO_3 (0.42 g, 3 mmol) and KI (0.03 g, 0.2 mmol) were then added and the resulting mixture was stirred at 140 °C for 3 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel (using dichloromethane as eluent) and recrystallization from a 1/1 hexane/ethanol mixture, yielding 0.82 g (95%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, $J = 8.8$ Hz, 2H, Ar−H), 7.67 (d, $J = 8.8$ Hz, 2H, Ar−H), 7.62 (d, $J = 8.1$ Hz, 2H, Ar−H), 7.50 (d, $J = 8.8$ Hz, 2H, Ar−H), 6.97 (d, $J = 8.8$ Hz, 2H, Ar−H), 6.88 (d, $J = 9.1$ Hz, 2H, Ar−H), 4.32 (q, $J = 7.2$ Hz, 2H, CH_2OCO), 4.01 (t, $J = 6.4$ Hz, 4H, OCH_2), 1.86−1.80 (m, 4H, CH_2), 1.57−1.53 (m, 4H, CH_2), 1.36 (t, $J = 7.2$ Hz, 3H, CH_3). IR (KBr): 2944, 2872, 2223, 1711, 1604, 1248 cm^{-1}.

4-[6-(4′-Cyanobiphenyl-4-yloxy)hexyloxy]benzoic acid.[23] Ethyl 4-[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoate (0.78 g, 1.8 mmol) obtained was refluxed in ethanol/THF (10 mL/10 mL) and aqueous KOH (0.3 g, 5 mmol, 1 mL) for 2 h. The solution was cooled to room temperature and acidified using aqueous HCl. The precipitated product was filtered and washed with water and ethanol. Because of the low product solubility, the product was not isolated further.

1H,1H,2H,2H-Heptadecafluoro-1-decyl 4-[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoate (1). A mixture of 4-[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoic acid (0.3 g, 0.72 mmol) and thionyl chloride (5 mL) was stirred at room temperature for 4 h. Thionyl chloride was then removed by evaporation under reduced pressure, leaving an off-white solid. The product was dissolved in 1,4-dioxane (6 mL). DMAP and 1H,1H,2H,2H-heptadecafluoro-1-decanol dissolved in 1,4-dioxane (3 mL) were added, and the resulting mixture was stirred at 80 °C for 5 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The residue was purified using column chromatography on silica gel using dichloromethane as eluent and reprecipitated with 1/10 chloroform/methanol to give the desired product, yielding 0.33 g (53%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, $J = 8.9$ Hz, 2H, Ar−H), 7.67 (d, $J = 8.5$ Hz, 2H, Ar−H), 7.62 (d, $J = 8.4$ Hz, 2H, Ar−H), 7.51 (d, $J = 8.7$ Hz, 2H, Ar−H), 6.97 (d, $J = 8.7$ Hz, 2H, Ar−H), 6.89 (d, $J = 8.8$ Hz, 2H, Ar−H), 4.58 (t, $J = 6.4$ Hz, 2H, CH_2OCO), 4.03−3.99 (m, 4H, OCH_2), 2.63−2.51 (m, 2H, CF_2CH_2), 1.86−1.80 (m, 4H, CH_2), 1.57−1.54 (m, 4H, CH_2). IR (KBr): 2940, 2870, 2233, 1716, 1608, 1255, 1204 cm^{-1}. Elemental anal. Calcd for $C_{36}H_{28}F_{17}NO_4$: C, 50.18; H, 3.28; N, 1.63. Found: C, 50.25; H, 3.34; N, 1.62.

1H,1H,2H,2H-Heptadecafluoro-1-decyl 3,4-bis[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoate (2). Compound **2** was synthesized by the same method as compound **1** from 3,4-bis[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoic acid (0.36 g, 0.5 mmol) and 1H,1H,2H,2H-heptadecafluoro-1-decanol (0.23 g, 0.5 mmol). Purification by column chromatography on silica gel using a 40/1 dichloromethane/ethyl acetate mixture as eluent and reprecipitation with 1/10 chloroform/methanol gave the desired product, yielding 0.19 g (33%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, $J = 8.4$ Hz, 4H, Ar−H), 7.64−7.57 (m, 5H, Ar−H), 7.51 (d, $J = 2.0$ Hz, 1H, Ar−H), 7.48 (d, $J = 8.7$ Hz, 4H, Ar−H), 6.95 (d, $J = 8.8$ Hz, 4H, Ar−H), 6.86 (d, $J = 8.6$ Hz, 1H, Ar−H), 4.58 (t, $J = 6.4$ Hz, 2H, CH_2OCO), 4.06 (t, $J = 6.8$ Hz, 2H, OCH_2), 4.04 (t, $J = 6.8$ Hz, 2H, OCH_2), 3.98 (t, $J = 6.4$ Hz, 4H, OCH_2), 2.62−2.53 (m, 2H, CF_2CH_2), 1.88−1.80 (m, 8H, CH_2), 1.56−1.54 (m, 8H, CH_2). IR (KBr): 2942, 2866, 2227, 1718, 1604, 1292, 1247, 1212, 821 cm^{-1}. Elemental anal. Calcd for $C_{55}H_{47}F_{17}N_2O_6$: C, 57.20; H, 4.10; N, 2.43. Found; C, 57.49; H, 3.93; N, 2.37.

1H,1H,2H,2H-Heptadecafluoro-1-decyl 3,4,5-tris[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoate (3). Compound **3** was synthesized by the same method as compound **1** from 3,4,5-tris[6-(4′-cyanobiphenyl-4-yloxy)hexyloxy]benzoic acid (0.38 g, 0.38 mmol) and 1H,1H,2H,2H-heptadecafluoro-1-decanol (0.18 g, 0.38 mmol). Purification by column chromatography on silica gel using a 40/1 dichloromethane/ethyl acetate mixture as eluent and reprecipitation with 1/10 chloroform/methanol gave the desired product, yielding 0.17 g (31%) of a white solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.63 (m, 6H, Ar−H), 7.60−7.57 (m, 6H, Ar−H), 7.49−7.45 (m, 6H, Ar−H), 7.27 (s, 2H, Ar−H), 6.95−6.91 (m, 6H, Ar−H), 4.58 (t, $J = 6.4$ Hz, 2H, CH_2OCO), 4.03−3.93 (m, 12H, OCH_2), 2.65−2.51 (m, 2H, CF_2CH_2), 1.87−1.74 (m, 12H, CH_2), 1.56−1.50 (m, 12H, CH_2). IR (KBr): 2942, 2867, 2225, 1720, 1604, 1248, 1211, 822 cm^{-1}. Elemental anal. Calcd for $C_{74}H_{66}F_{17}N_3O_8$: C, 61.37; H, 4.59; N, 2.90. Found: C, 61.69; H, 4.80; N, 2.86.

Liquid-Crystalline and Physical Properties. The initial phase assignments and corresponding transition temperatures for the final products were determined by optical polarized light microscopy using a polarizing microscope (Optiphot-pol; Nikon Corp.) equipped with a hot stage and FP80 control processor (FP82; Mettler Inst. Corp.). The heating and cooling rates were 5 °C min^{-1}. The photomicrographs were taken using a camera (Olympus Digital Camera C-5050 ZOOM; Olympus Optical Co. Ltd.) in conjunction with a polarizing microscope (Optiphot-pol; Nikon Corp.). Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC) with a calorimeter (DSC6200; Seiko Instruments Inc.). The materials were studied at a scanning rate of 5 °C min^{-1} after being encapsulated in aluminum pans. The X-ray diffraction patterns of the sample on cooling process were obtained using a real-time X-ray diffractometer (D8 Discover; Bruker AXS GmbH) equipped with a hot stage and FP80 control processor (FP82; Mettler Inst. Corp.). A sample was introduced into a thin glass capillary tube (diameter: 1.0 mm) that was placed in a custom-made temperature stabilized holder (stability within ±0.1 °C). The X-ray apparatus was equipped with a cross-coupled Göbel mirror on platform system with a two-dimensional position-sensitive proportional counter (PSPC) detector (HI-Star; Bruker AXS GmbH). X-rays was generated at 40 kV and 40 mA, and a parallel Cu Kα X-ray beam was used to irradiate the sample. Each diffraction pattern was obtained using the PSPC detector at a camera distance of 150 mm for a short counting time of 5 min. We waited for about 10 min before starting the measurements at each temperature.

Results and Discussion

Transition temperatures and transition enthalpies of the amphiphilic oligomers determined by optical microscopy and differential scanning calorimetry (DSC) are shown in Table 1.

Compound **1**, with one cyanobiphenyl mesogenic moiety, showed the phase sequence Cr−SmC−Iso on heating. The SmC phase was identified by a broken fan texture in the planarly aligned region and a schlieren texture in the homeotropically aligned region. Compound **2** possessing two cyanobiphenyl mesogenic moieties showed the phase sequence Cr−Col−SmA−Iso on heating. Upon cooling, a

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Table 1. Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}; in square brackets) of Compounds 1−3[a]

compound	Phase transition temperatures (°C) [ΔH / kJ mol^{-1}]^{b}
1	$\mathrm{Cr} \underset{87.4\ [-36.6]}{\overset{110.3\ [39.4]}{\rightleftarrows}} \mathrm{SmC} \underset{139.1\ [-11.5]}{\overset{140.2\ [11.8]}{\rightleftarrows}} \mathrm{Iso}$
2	$\begin{matrix}\mathrm{Cr}\\ \mathrm{G}\end{matrix} \underset{10.1}{\overset{62.2\ [18.7]}{\rightleftarrows}} \mathrm{Col} \underset{115.7\ [-3.4]}{\overset{134.2\ [2.5]}{\rightleftarrows}} \mathrm{SmA} \underset{169.6\ [-10.3]}{\overset{170.6\ [10.6]}{\rightleftarrows}} \mathrm{Iso}$
3	$\begin{matrix}\mathrm{Cr}\\ \mathrm{G}\end{matrix} \underset{9.0}{\overset{83.2\ [34.5]}{\rightleftarrows}} \mathrm{Cub} \underset{135.9\ [-3.5]}{\overset{141.1\ [2.8]}{\rightleftarrows}} \mathrm{SmA} \underset{154.2\ [-5.4]}{\overset{154.9\ [5.7]}{\rightleftarrows}} \mathrm{Iso}$

[a] Abbreviations: Cr = crystalline solid state; G = glassy state; Iso = isotropic liquid state; SmC = smectic C phase; SmA = smectic A phase; Col = columnar phase; Cub = cubic phase. [b] Determined by differential scanning calorimetry at a scanning rate of 5 °C min^{-1}.

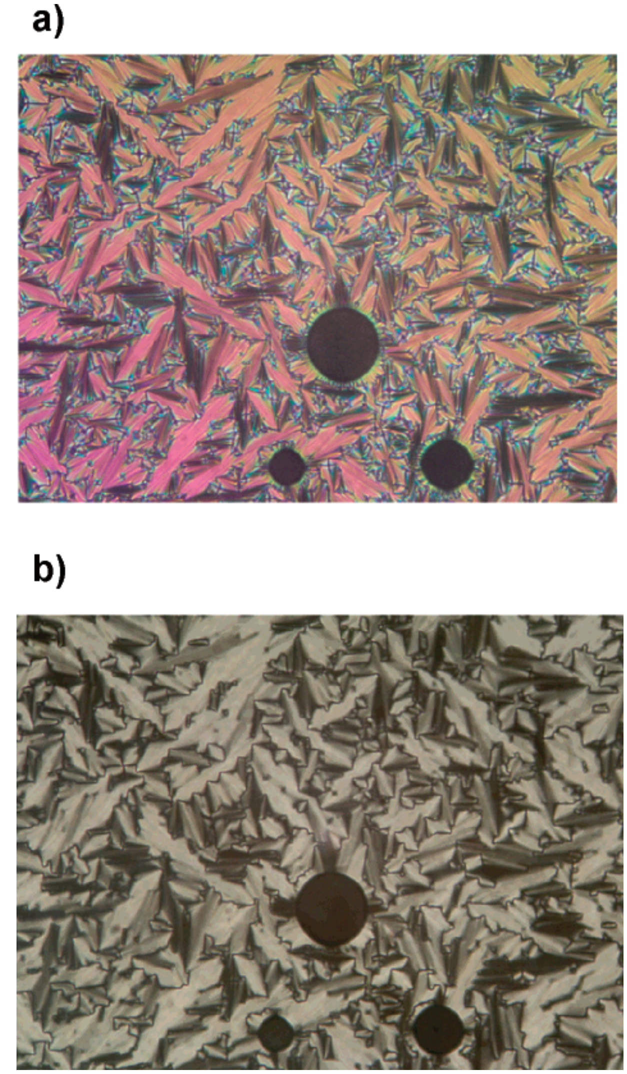

Figure 4. Optical textures of (a) the SmA phase at 168.5 °C and (b) the Col phase at 115 °C for compound **2**.

glassy transition was observed at 10.1 °C by DSC, but not a recrystallization. Figure 4 shows optical textures of the SmA and Col phases. In the SmA to Col phase transition, the fans of the SmA phase were broken slowly; the weakly birefringent fan texture was observed in the Col phase.[24]

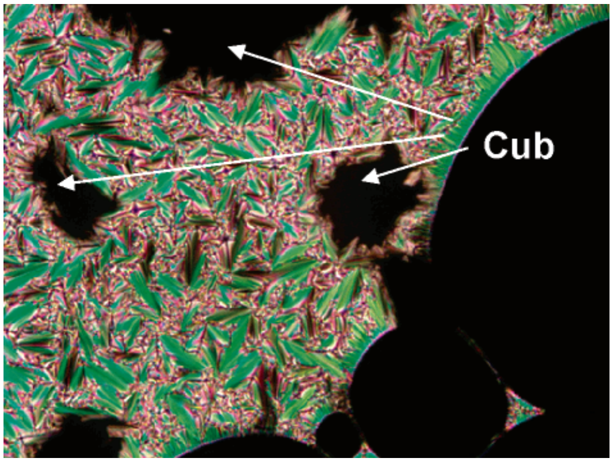

Figure 5. The optical texture of the SmA−Cub phase transition at 135.8 °C for compound **3**.

Compound **3**, possessing three cyanobiphenyl mesogenic moieties, showed the phase sequence of Cr−Cub−SmA−Iso on heating. During the cooling process, a glassy transition was observed at 9.0 °C. Figure 5 shows the optical texture of the SmA-to-Cub phase transition on cooling. In the fan textures of the SmA phase, highly viscous optically isotropic domains grew rapidly.

Investigation of the miscibility between the SmC, Col, and Cub phases might be useful for clarifying the structures of these observed mesophases for compounds **1**−**3**. For example, it was reported that a hexagonal columnar phase was induced by the mixing of polyhydroxy amphiphile with SmA phase and that with micellar cubic phase.[15] Therefore, we performed miscibility studies for compounds **1**−**3** (see Figure 6).

For the miscibility phase diagram between compounds **1** and **3**, the SmC phase of compound **1** and the Cub phase of compound **3** disappeared around the middle composition region; a columnar phase was not induced. For the miscibility phase diagram of compounds **2** and **3**, the phase sequence Iso−SmA−Cub−Col was observed for mixtures containing 25−30 wt % compound **3**. The Cub phase of compound **3** appeared between the lamellar (SmA phase) and columnar phases, suggesting that the Cub phase has a bicontinuous structure. A few structural modifications of these compounds were performed and the transition properties were investi-

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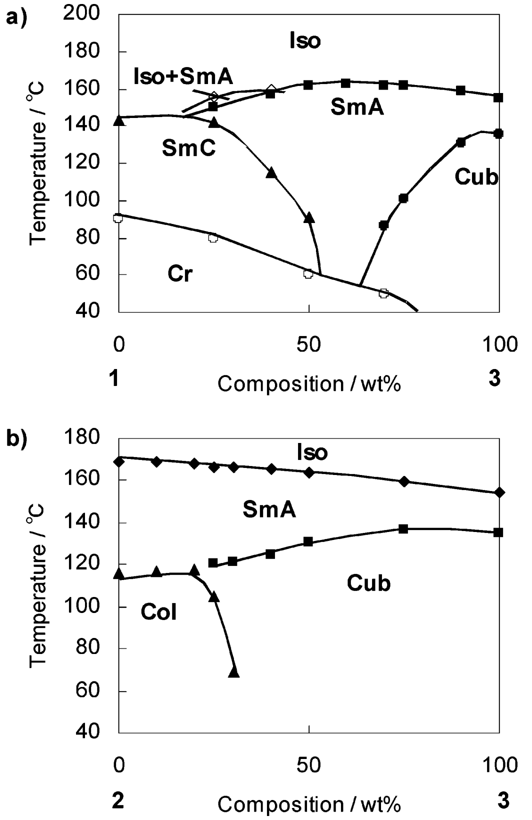

Figure 6. Miscibility phase diagrams (a) between compounds **1** and **3**, and (b) between compounds **2** and **3**.

gated.[25] The obtained results are consistent with the present assignments of the above phases. In a following paper, we will report further structure−property relationships.

Figure 7 shows X-ray diffraction profiles in the small angle region of compound **2** in the SmA and Col phases. We have never succeeded in preparation of completely oriented samples suitable for two-dimensional X-ray diffraction measurements. Therefore, we discuss the phase structures using one-dimensional X-ray diffraction. In the SmA phase at 130 °C, two sharp reflections, $2\theta = 1.38$ and 1.78°, were observed in the small-angle region, respectively corresponding to spacings of 63.9 and 49.6 Å (see Figure 7a). The origin of the two reflections in the SmA phase remains unclear. However, some examples of observations of two reflections of the small-angle region were reported in the modulated SmA phases[26] and the incommensurate SmA phases.[22,27] The appearance of the second-order peaks in the small-angle region indicates the formation of well-defined periodic structures. The molecular length of compound **2** was estimated from the MM2 model to be 39.7 Å. The result that the obtained spacings were longer than the molecular length suggests that the SmA phase has an interdigitated structure.[28] Figure 8a shows a possible model for the SmA phase. Here, the SmA phase is considered to be composed of three distinct sublayers of aromatic cores, aliphatic chains, and fluorinated chains because of the incompatibility of these segments.[29−31] Thus, the obtained spacing of 63.9 Å was found to correspond to the layer spacing of the interdigitated structure with intercalation of the fluorinated alkyl chains However, the spacing of 49.6 Å was not assignable to any molecular arrangements. In the Col phase at 110 °C, five reflections, $2\theta = 1.13$, 1.47, 1.77, 2.99, and 3.51°, were observed (Figure 7b), which can be indexed on the basis of a rectangular 2D lattice with lattice parameters $a = 156.2$ Å and $b = 64.9$ Å, as shown in Table 2. Figure 8b shows a possible arrangement of the molecules in the columnar phase. In the columnar phase, the fluid fluorinated alkyl chains are segregated in the central region of each column, surrounded by the outer region composed of the aliphatic spacers and cyanobiphenyl mesogenic cores. There is another arrangement in which the cyanobiphenyl mesogenic cores are pointing into the middle. However the reverse arrangement is unlikely, because the oligomers exhibited a phase sequence of lamellar−columnar phases by increasing the number of the cyanobiphenyl moieties.

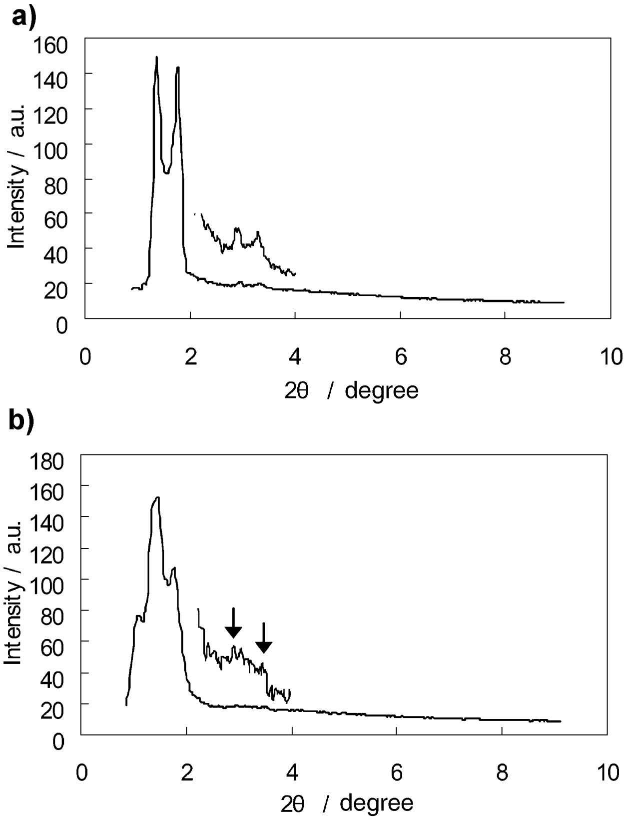

Figure 7. X-ray diffraction patterns of compound **2** in (a) the SmA phase at 130 °C and (b) the Col phase at 110 °C; expansions are included for clarity.

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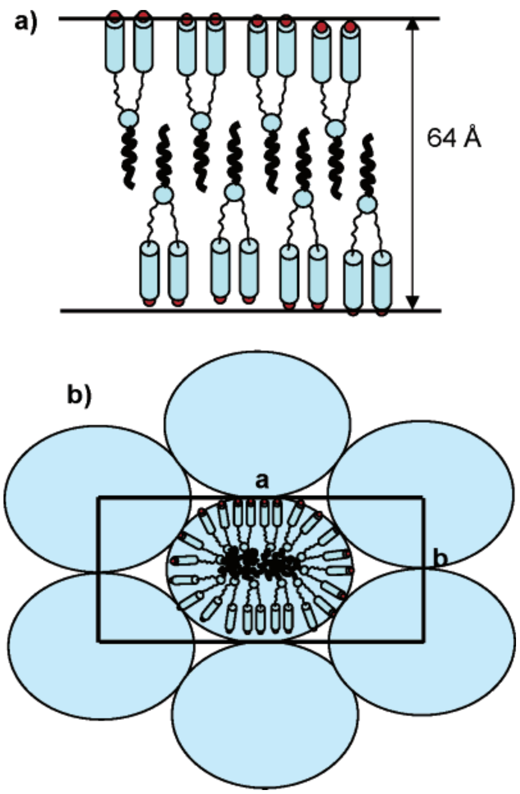

Figure 8. Arrangement suggested for compound **2** in (a) the SmA phase and (b) the rectangular columnar phase with lattice parameters a = 156.2 Å and b = 64.9 Å.

Table 2. Observed Reflections in the Columnar Phase of Compound 2

θ_{exp} (deg)	$h\,k\,l$	θ_{calcd} (deg)
0.565	200	0.565
0.735	110	0.735
0.885	210	0.885
1.495	220	1.476
1.755	420	1.765

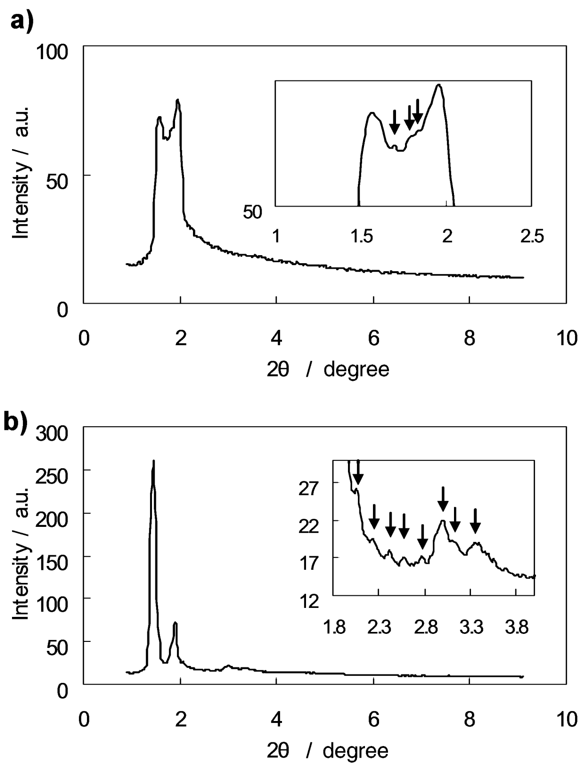

Figure 9. X-ray diffraction patterns of compound **3** in (a) the SmA phase at 150 °C and (b) the Cub phase at 100 °C; expansions are included for clarity.

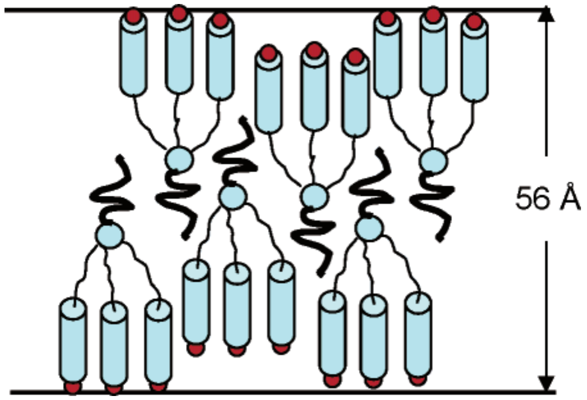

Figure 10. Arrangement suggested for compound **3** in the SmA phase.

Figure 9 shows X-ray diffraction profiles in the small-angle region of compound **3** in the SmA and Cub phases. In the SmA phase at 150 °C, two broad reflections, $2\theta = 1.58$ and 1.96°, were observed in the small angle region, corresponding, respectively, to spacings of 55.8 and 45.0 Å (see Figure 9a). The absence of the second-ordered reflections indicates weak periodicities. In addition, a few reflections appeared to exist between the two reflections and a diffuse asymmetric tail spread around the Bragg peaks, indicating the possibility of fluctuation of the layer structure. The several weak reflections except the two sharp peaks can result from perforated lamellae. The diffuse tail originates from the undulation of lamellae.[32] The molecular length was estimated from the MM2 model to be 36.6 Å. The obtained spacings, which were longer than the molecular length, suggest the formation of an interdigitated structure.[28] Figure 10 shows a possible model for the SmA phase. In polyphilic block molecules, the incompatible segments tend to segregate into the different sublayers in the SmA phase. However, in pronounced tapered molecules such as those of compound **3**, steric effects can override the segregation of the incompatible segments.[30] Therefore, intercalation of the fluorinated chains and the aliphatic spacers is considered to be generated. The result is that the layer spacing of compound **3** is shorter than that of compound **2**. Furthermore, the competition of the steric effect and the segregation effect might give rise to fluctuation of layer spacing. In the Cub phase at 110 °C, many reflections were observed in the small-angle region (see Figure 9b). The Bragg angles of the observed reflections match the proportions of $\sqrt{4}$, $\sqrt{7}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{11}$, $\sqrt{13}$, $\sqrt{15}$, $\sqrt{18}$, $\sqrt{19}$, and $\sqrt{22}$. The ratios $\sqrt{7}$ and $\sqrt{15}$ are not compatible with any cubic lattices. Therefore, the sequence of numbers must be doubled.[33] The obtained ratios are $\sqrt{8}$, $\sqrt{14}$, $\sqrt{16}$, $\sqrt{20}$, $\sqrt{22}$, $\sqrt{26}$, $\sqrt{30}$, $\sqrt{36}$, $\sqrt{38}$, and $\sqrt{44}$, which engenders the Miller indices cited in Table 3. The

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Table 3. Observed Reflections in the Cubic Phase of Compound 3

θ_{exp} (deg)	*h k l*	θ_{calcd} (deg)
0.72	220	0.72
0.95	321	0.95
1.03	400	1.02
1.12	420	1.12
1.21	332	1.20
1.29	510, 431	1.30
1.38	521	1.39
1.51	600, 442	1.53
1.57	611, 532	1.57
1.68	622	1.69

given indexing with the absence of reflections of lower Miller indices (100), (110), (111), (200), and (210) matches the space group *Ia*3*d*, which represents a bicontinuous cubic phase built by two interpenetrating networks of branched cylinders.[3] The cell parameter is estimated to be $a = 173.7 \pm 2.5$ Å.

In the amphiphilic polyhydroxy derivatives, the phase sequence SmA−Cub_V−Col_h−Cub_I was obtained when the number and length of the aliphatic chains was increased to make them similar to surfactants of the lyotropic systems.[14,15] Moreover, the tetracatenar compounds showed the phase sequence SmC−Cub_V−Col_h on increasing the length of the terminal aliphatic chains.[12e,13f] In contrast, the amphiphilic liquid-crystalline oligomers **1**−**3** in this paper showed a different phase sequence, SmC−Col−Cub_V, on increasing the cyanobiphenyl mesogenic moieties; the sequence Col−Cub_V is opposite that of the ordinary sequence. The SmA to Col transition of compound **2** is explainable by (1) the interfacial curvature between the region of the fluorinated alkyl chains and that of the cyanobiphenyl cores and aliphatic alkyl spacers, and (2) layer deformation induced by the λ-shaped molecule. Let us consider the unusual SmA-to-Cub_V transition of compound **3** instead of a SmA-to-Col transition or a SmA-to-Cub_I transition. The peripheral three cyanobiphenyl moieties are considered to play an important role in the molecular assembly of compound **3**. In contrast to the peripheral aliphatic chains, which are flexible and behave as a fluid in the polyhydroxy derivatives[14,15] and tetracatenar systems,[12e,13f] the peripheral cyanobiphenyl cores are rigid and have strong dipole moments in compound **3**. Results of an XRD study suggest that the SmA phase of compound **3** has a fluctuated layer structure. The competition of the steric effect attributable to the pronounced taper shape and the segregation effect of compound **3** might give rise to that fluctuation. On the other hand, an undulatory deformation mode for a nonequilibrium lamellar structure is known to exist as the unstable transient state between the lamellar and the Cub (Gyroid with a space group *Ia*3*d*) phases in some diblock copolymers.[34] Recently, fluctuations of lamellar structure prior to a lamellar-to-gyroid transition in a nonionic surfactant system was observed.[35] An interesting explanation for the fluctuations has been proposed as that (1) amplitude-modulation fluctuations appear in lamellae, (2) modulation fluctuations increase their amplitude as the temperature approaches the transition, and (3) they develop to a perforation fluctuation layer as an equilibrium structure.[35] Consequently, the fluctuated lamellar structure in the SmA phase of compound **3** is thought to be stabilized by increasing the number of the cyanobiphenyl mesogenic moiety, which can produce the Cub_V phase. This mechanism of the formation of the Cub_V phase is a novel one in the low molecular thermotropic liquid-crystalline systems.

Conclusion

In summary, the newly designed amphiphilic liquid-crystalline oligomers were found to realize the unusual phase sequence of SmC−Col−Cub_V with increasing cyanobiphenyl mesogenic moieties. It is noteworthy that the interfacial fluctuations caused by the competition of the steric effect and the segregation effect in the SmA phase of compound **3** might engender the formation of the Cub_V phase.

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