Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Feb 2010

To cite this article: Yuko Kamikawa, Naho Fujimoto, Bertrand Donnio, Daniel Guillon & Takashi Kato (2010): Self-Assembled Structures of Liquid-Crystalline Oligopeptide Dimers, Molecular Crystals and Liquid Crystals, 516:1, 132-143

To link to this article: http://dx.doi.org/10.1080/15421400903400860

Mol. Cryst. Liq. Cryst., Vol. 516: pp. 132–143, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903400860

Self-Assembled Structures of Liquid-Crystalline Oligopeptide Dimers

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We have prepared a series of thermotropic liquid-crystalline oligopeptide dimers based on dendritic oligo(glutamic acid)s. The synthesized oligopeptide dimers form thermally stable columnar liquid crystals. Self-assembled structures of the columnar liquid crystals varied with the spacer length and molecular chirality of the oligopeptide residues.

Keywords Amino acids; hydrogen bonds; liquid crystals; self-assembly

Introduction

Liquid-crystalline (LC) materials based on molecular self-assembly have attracted a great deal of attention in nanoscience and advanced technologies [1–4]. Molecules with a variety of shape and flexibility can form liquid crystalline structure [1–8]. Taking advantage of biomimetic self-assembly approach, amino acids and polypeptides have been widely used as building blocks for functional self-assembled liquid-crystalline materials [9–16], as well as nanofibers [17–20], and nanotubes [21]. Chemically modified polypeptides such as poly(γ-benzyl L-glutamate) have been studied for the past decades as thermotropic and lyotropic liquid crystals [9–11]. Nevertheless, only a few examples have been reported for LC materials based on low molecular weight amino acids [12,15]. To induce liquid crystallinity, materials

This work was financially supported by Grant-in-Aid for Scientific Research (A) (No. 19205017) (T.K.) from the Japan Society for the Promotion of Science (JSPS) and a Grant-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology. Y.K. is thankful for financial support from the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

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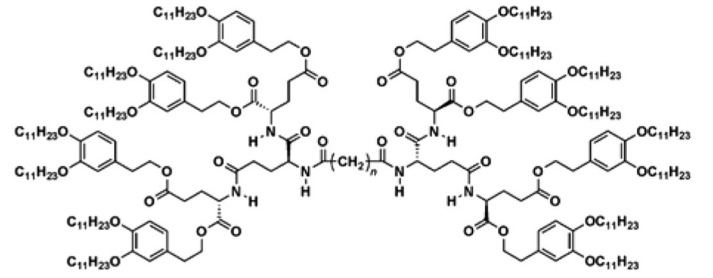
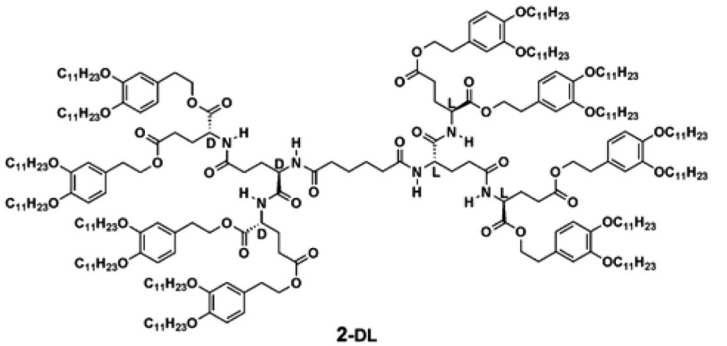
should keep the good balance between ordering and disordering forces to afford anisotropic structures with dynamic fluid properties.

Our intention here is to develop new thermotropic liquid-crystalline materials based on oligopeptides. Recently, we have reported that fan-shaped oligo(glutamic acid)s with dendritic branched structures form self-assembled columnar liquid crystals [12]. Herein we report on the syntheses and liquid-crystalline properties of the dendritic oligopeptide dimers. LC dimers and oligomers are made of covalently bonded two or more mesogenic units and often exhibit different LC properties from the single mesogenic building blocks [22,23]. Intensive researches have been made for developing LC dimers with identical or combination of different mesogenic units, LC oligomers, and dendritic liquid crystals [5,23–27]. The LC oligomers were first investigated as model compounds for the LC polymers [24]. Thus LC



1-3 (**1**: $n = 3$; **2**: $n = 4$; **3**: $n = 10$)



2-DL

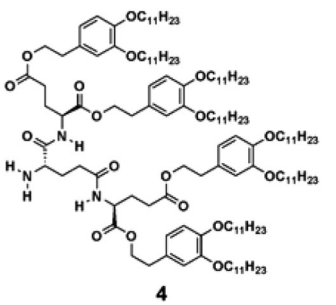


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Figure 1. Molecular structures of the oligopeptide dimers **1-3** ($n = 3$, 4, 10), heterochiral dimer **2-DL**, and the fan-shaped oligoglutamate **4**.

dimers of oligopeptides may fill the gap between conventional LC polypeptides and low molecular weight liquid crystals based on amino acids. We focus on the LC dendritic oligo(glutamic acid)s as a building block, and covalently connect two fan-shaped oligoglutamates by alkyl amide linkages (Fig. 1). LC dimers **1-3** were prepared and their LC properties were examined. Compounds **1-3** are made up of two identical oligo(L-glutamic acid)s block **4** with different alkyl spacer length ($n = 3$, 4, 10). Compound **2-DL** is a diastereomer of compound **2** and has the oligo(L-glutamic acid)s on one end of the spacer and the oligo(D-glutamic acid)s on the other end (Fig. 1).

Experimental

General Methods and Materials

All starting materials were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck silica gel plates (Silica Gel F_{254}), and silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (Silica Gel 60, spherical, 40–50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. ^{1}H NMR spectra were recorded on a JEOL JNM-LA400. Chemical shifts of ^{1}H NMR signals were expressed in parts per million (δ) using internal standard Me_4Si ($\delta = 0.00$). Coupling constants, J, were reported in Hertz (Hz). Mass spectra were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out on a perkin-Elmer CHNS/O 2400 apparatus. DSC measurements were conducted on a Mettler DSC 30 to determine the thermal transitions (scanning rate: 10°C min^{-1}). A polarizing optical microscope Olympus BH-2 equipped with a Mettler FP82HT hot stage was used for visual observation. X-ray diffraction measurements were carried out on a Rigaku RINT 2100 diffractometer with a heating stage using Ni-filtered CuKα radiation.

Spectroscopy: The UV-Vis absorption spectra of the bulk samples were recorded on a Agilent 8453 spectrophotometer using rectangular quartz plates with 200 μm thickness. Circular dichroism spectra were recorded on a Jasco J-820 spectropolarimeter. Variable-temperature CD spectra were obtained using a Mettler FP82HT hot stage. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus in CaF_2 plates.

Synthesis

Compound **4** was synthesized following the literature procedure [12,13].

General Method: 1–3

Two-necked round bottom flask was flamed dried, then added **4** (0.184 g, 0.084 mmol) dissolved in dry THF (10 ml). Triethylamine (12 μl, 0.084 mmol) was added slowly to the flask, followed by slow addition of adipoyl chloride (5.8 μl, 0.040 mmol) while stirring. The mixture was stirred for 3 h in an Ar atmosphere. The solvent was evaporated, and the residue was added to chloroform/water = 1/1 mixture, and extracted three times with chloroform. The collected organic fractions were washed with sat. NaCl aq., dried over Na_2SO_4, and the solvent was removed under reduced pressure. The

residue was purified by silica gel column chromatography (hexane/ethyl acetate, 1/1) followed by GPC to yield **2** (0.149 g, 0.033 mmol, 83%) as a colorless solid.

Synthesis of Compound 2-DL

Two-necked round bottom flask was flamed dried, then added **4-D** (0.110 g, 0.05 mmol) dissolved in dry THF (10 ml). Triethylamine (35 µl, 0.25 mmol) was added slowly to the flask, followed by slow addition of adipoyl chloride (36 µl, 0.25 mmol) while stirring. The mixture was stirred for 3 h in an Ar atmosphere. The solvent was evaporated, and the residue was added to chloroform/water = 1/1 mixture, and extracted three times with chloroform. The collected organic fractions were washed with sat. NaCl aq., dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by GPC to yield monocarboxylic acid derivative 0.073 g, 0.032 mmol, 63%) as a colorless solid. The material was then dissolved in dry CH_2Cl_2 (20 ml), added **4-L** (0.083 g, 0.038 mmol), and EDC (0.012 g, 0.063 mmol) while stirring. The solution was stirred under Ar atmosphere for 12 h. The reaction mixture was extracted three times with chloroform. The collected organic fractions were washed with sat. NaCl aq., dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (gradient of hexane/ethyl acetate, 1/1 to 2/5) followed by GPC to yield **2-DL** (0.069 g, 0.015 mmol, 49%) as a colorless solid.

1: Yield 69%, as a colorless solid.

(Found C, 73.7; H, 10.7; N, 2.1. $C_{275}H_{466}N_6O_{38}$ requires C, 74.0; H, 10.5; N, 2.0%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (48 H, m), 1.20–1.50 (256 H, m), 1.71–1.86 (34 H, m), 2.10–2.50 (28 H, m), 2.80–2.95 (16 H, m), 3.84–4.00 (32 H, m), 4.05–4.35 (20 H, m), 4.60–4.70 (2 H, m), 6.70–6.85 (24 H, m), 7.81 (2 H, d, *J* 8.0), 8.27 (2 H, d, *J* 8.0); IR (KBr) 3288, 3060, 2924, 2854, 1737, 1639, 1588, 1543, 1515, 1468, 1427, 1389, 1263, 1232, 1168, 1140, 1044, 1025 cm^{-1}; *m/z* (MALDI) 4488 (calcd $[M+Na]^+ = 4484.5$ Mol. wt. = 4487.7).

2: Yield 83%, as a colorless solid.

(Found C, 73.8; H, 10.8; N, 1.9. $C_{276}H_{468}N_6O_{38}$ requires C, 74.0; H, 10.5; N, 1.9%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (48 H, m), 1.20–1.50 (260 H, m), 1.70–1.85 (32 H, m), 2.10–2.50 (28 H, m), 2.80–2.95 (16 H, m), 3.84–3.99 (32 H, m), 4.20–4.40 (20 H, m), 4.60–4.70 (2 H, m), 6.70–6.85 (24 H, m), 7.70 (2 H, d, *J* 8.0), 8.03 (2 H, d, *J* 8.0); IR (KBr) 3303, 3047, 2955, 2923, 2852, 1735, 1638, 1608, 1589, 1519, 1467, 1427, 1391, 1263, 1234, 1192, 1170, 1141, 1069, 1049, 1021 cm^{-1}; *m/z* (MALDI) 4502 (calcd $[M+Na]^+ = 4498.5$ Mol. wt. = 4501.7).

3: Yield 70%, as a colorless solid.

(Found C, 74.1; H, 10.6; N, 1.8. $C_{282}H_{480}N_6O_{38}$ requires C, 74.2; H, 10.6; N, 1.8%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (48 H, m), 1.20–1.50 (272 H, m), 1.70–1.85 (32 H, m), 2.10–2.50 (28 H, m), 2.80–2.95 (16 H, m), 3.90–4.00 (32 H, m), 4.10–4.40 (20 H, m), 4.62–4.70 (2 H, m), 6.70–6.85 (24 H, m), 7.66 (2 H, d, *J* 8.0), 8.02 (2 H, d, *J* 8.0); IR (KBr) 3292, 3069, 2923, 2852, 1737, 1640, 1588, 1541, 1516, 1468, 1427, 1389, 1339, 1263, 1234, 1189, 1167, 1139, 1069, 1045, 1024, 1001 cm^{-1}; *m/z* (MALDI) 4586 (calcd $[M+Na]^+ = 4582.6$ Mol. wt. = 4585.9).

2-DL: Yield 63%, as a colorless solid.

(Found C, 73.1; H, 10.8; N, 2.1. $C_{276}H_{468}N_6O_{38}$ requires C, 74.0; H, 10.5; N, 1.9%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (48 H, m), 1.20–1.50 (260 H,

m), 1.72–1.86 (32 H, m), 2.10–2.50 (28 H, m), 2.80–2.92 (16 H, m), 3.90–4.00 (32 H, m), 4.05–4.35 (20 H, m), 4.55–4.65 (2 H, m), 6.70–6.85 (24 H, m), 7.68 (2 H, d, *J* 8.0), 8.03 (2 H, d, *J* 8.0); IR (KBr) 3303, 3047, 2954, 2920, 2852, 1734, 1645, 1608, 1590, 1519, 1467, 1428, 1390, 1339, 1264, 1234, 1192, 1168, 1141, 1071, 1028, 999 cm^{-1}; *m/z* (MALDI) 4502 (calcd $[M+Na]^+ = 4498.5$ Mol. wt. = 4501.7).

Results and Discussion

Liquid-Crystalline Properties of Oligo(glutamic acid)s Dimers

Oligo(glutamic acid) dimers **1-3** and **2-DL** as a diastereomer of **2** were prepared. Table 1 summarizes the thermal properties of the compounds and the fan-shaped oligo(glutamic acid) unit **4**. Phase transition temperatures were determined by DSC and visual observation (Table 1, Fig. 2). Dimers **1-3** show at least 20°C higher isotropization temperatures than that of **4**. The melting points of the dimers are also lower than that of **4**, except for compound **3**. Binding two oligo(glutamic acid) units into dimers contributes to thermal stabilization of the LC phases. Compound **2** shows a columnar phase from 69°C to 143°C, whereas compound **1** forms a columnar phase from 54°C to 129°C. The increase of alkyl spacer length from $n = 4$ to $n = 10$ results in slight destabilization of the LC phase since compound **3** exhibits a columnar phase from 76°C to 119°C. The combination of chirality of the peptide moieties also affects LC properties. Compound **2-DL**, the diastereomer of **2**, exhibits a columnar LC phase over 100°C from 31°C to 131°C. It is of interest that odd-even numbers of alkyl spacers, alkyl spacer length, and combination of molecular chirality, all these factors influence thermal properties of the LC dimers. The alkyl spacers from $n = 3$ to 10 are rather short compared to the size of the oligoglutamate residues. The short alkyl spacers may tightly bind two bulky oligopeptide units and more or less distort them from an energetically favored arrangements. The oligoglutamate units reported here are flexible enough to adapt some structural distortion and can maintain LC structures with wide structural variations.

IR spectra of compounds **1-3** were obtained to study the role of hydrogen bonds of the peptide moieties in LC states (Table 2). On cooling down from isotropic melts, all of the compounds show blue shift of the amide I and amide A bands (Table 2). For example, the amide I band of compound **1** shifts from 1674 to 1643 cm^{-1} around Iso-LC transition but further cooling below the LC-Cr transition does not induce

Table 1. Thermal properties and X-ray results of oligo(glutamic acid)s derivatives **1–4** on the second heating

Compounds	Phase transition temperature (°C)					Phase	X-ray results		
							T(°C)	*a*	*b*(Å)
1	Cr	54	Col_r	129	Iso	Col_r	100	77.4	26.2
2	Cr	69	Col_r	143	Iso	Col_r	100	73.6	25.2
2-DL	Cr	31	Col_r	131	Iso	Col_r	100	68.4	55.0
3	Cr	76	Col_h	119	Iso	Col_h	100	60.0	
4	Cr	74	Col_h	88	Iso	Col_h	80	42.8	

Cr: crystalline; Col_h: hexagonal columnar; Col_r: rectangular columnar; Iso: isotropic.

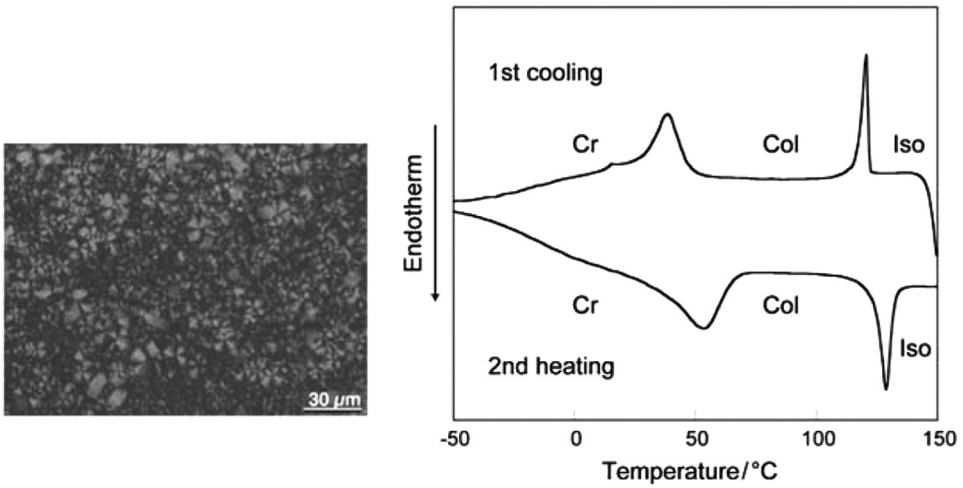

Figure 2. (a) Polarized optical photomicrograph of **1** at 91°C on cooling. (b) DSC traces of compound **1**. Heating rate: 10°C/min.

noticeable change (Fig. 3). The amide I band of compound **4** is broad and contains several peaks at 1642, 1655, 1678 cm^{-1}[12]. This observation suggests that hydrogen bonds of oligoglutamate moieties are dynamic and in equilibrated states between hydrogen-bonded and dissociated states for the fan-shaped unit **4**. In contrast, amide I and amide A bands for compounds **1-3** are much sharper and contain single peaks. The results show that all the amide groups of the oligopeptide dimers contribute to intra- and/or intermolecular hydrogen bonds. The resulting hydrogen-bonded structures afford columnar arrangements of the oligopeptides and also contribute to thermal stabilization of the LC phases for **1-3** (Fig. 3).

X-ray Structural Analysis

XRD profiles of **1–3** are shown in Figure 4. Compounds **1** and **2** form rectangular columnar phases attributed to *p2gg* space group (Table 1, Fig. 4a,b) [28,29]. Compound **2-DL** also forms a rectangular columnar phase with a two dimensional lattice larger than that of **2** (Table 1, Fig. 4b,d). Compound **3** exhibits a hexagonal

Table 2. IR results of the compounds **1-3**

Compounds	T/°C	*Amide* I/cm^{-1}	*Amide* A/cm^{-1}	T/°C	*Amide* I/cm^{-1}	*Amide* A/cm^{-1}
1	110 (LC)	1643	3289	140 (Iso)	1674	3324
2	110 (LC)	1638	3293	150 (Iso)	1678	3355
3	110 (LC)	1639	3291	130 (Iso)	1685	3369

LC: liquid-crystalline; Iso: isotropic.

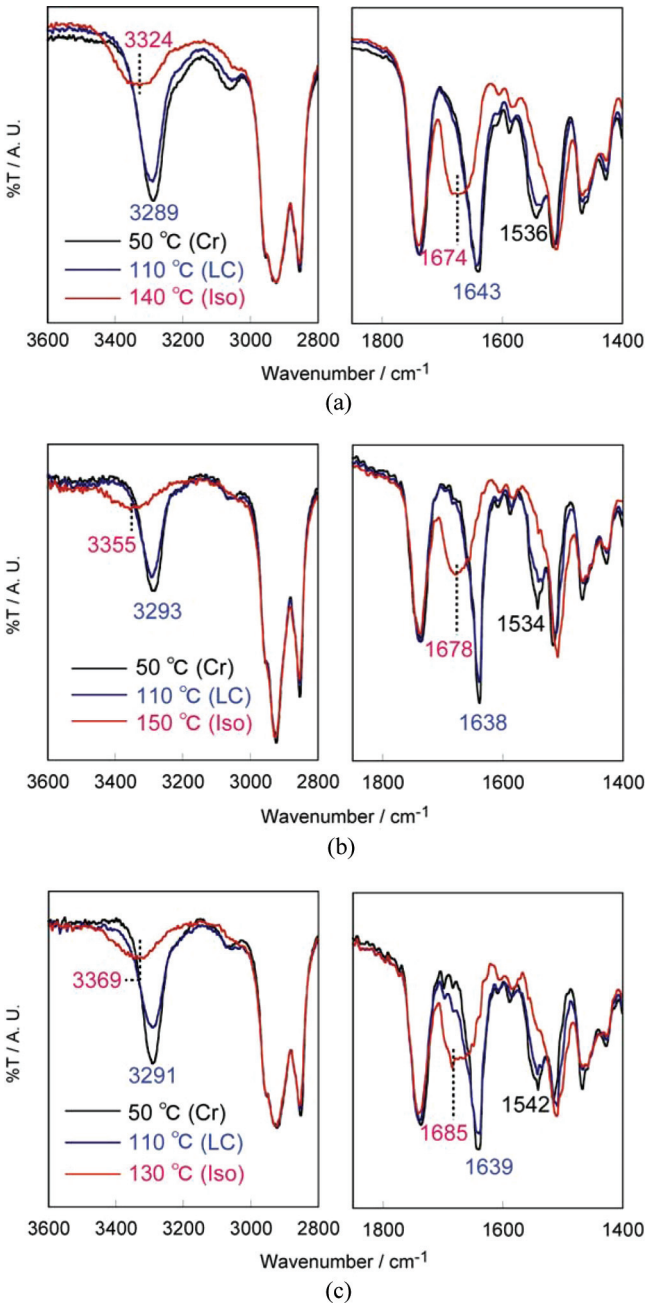

Figure 3. VT-IR spectra of (a) **1**, (b) **2**, and (c) **3**.

columnar phase with the column diameter of 60 Å (Table 1, Fig. 4c). Z values for each lattice are 2 for the *p2gg* rectangular phase and 1 for the *p6mm* hexagonal phase. Taking the density of the compounds as 1.0 g/cm^3, number of molecules per column stratum are calculated as follows (Fig. 5).

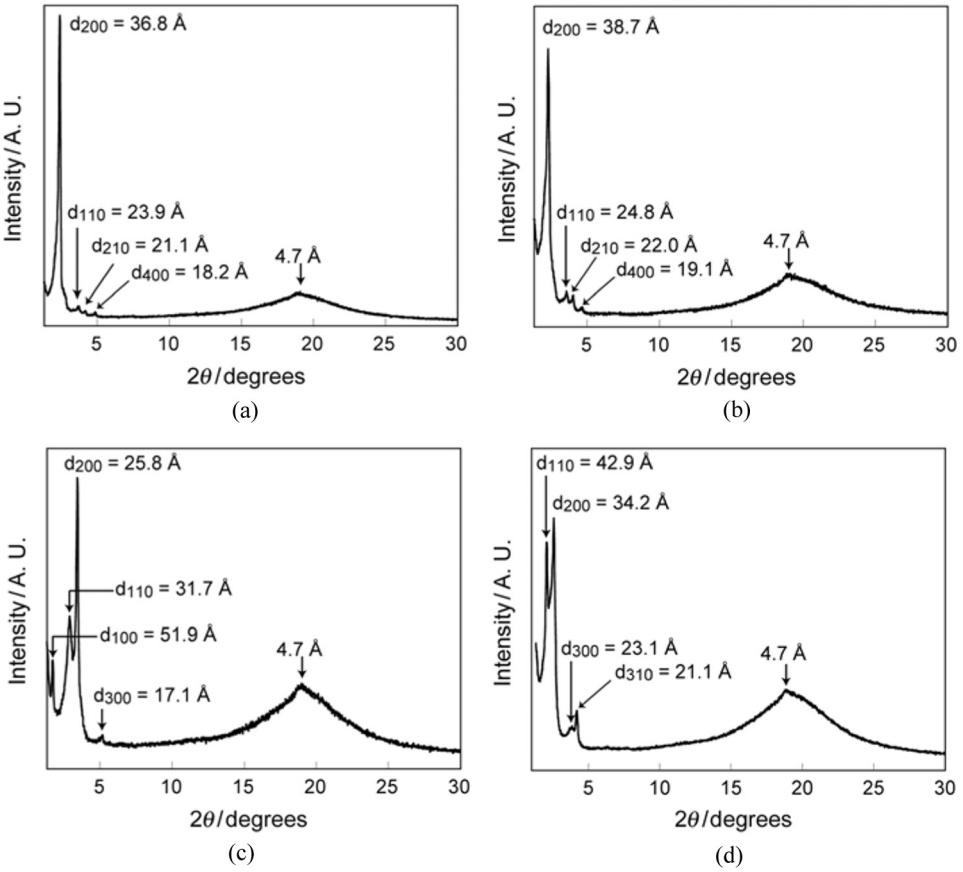

Figure 4. XRD profiles of compounds **1** (a), **2** (b), **3** (c), and **2-DL** (d) measured at 100°C.

$$Z = \frac{\rho N_A V}{\mu M}$$

$$V = abc \sin \gamma$$

(ρ: density; N_A: avogadro's number; V: segmental volume of the columnar stratum; μ: number of molecules per V; M: molecular mass; a, b, c, γ = lattice constants).

If you take lattice constant $c = 4.7$ Å (the band of hallow), the columnar assemblies of **1** and **2** consist of 0.6 molecules per segment V, whereas those of **2-DL** are composed of 1.2 molecules per V. These results indicate that compound **2-DL** takes flat conformation and stacks with normal hallow spacings of 4–5 Å in the columnar phases (Figs. 5, 6). Compounds **1** and **2** also form rectangular columnar phases with smaller two-dimensional lattice structures. The distance between piled up molecules should be longer than that of **2-DL**. For example, to fulfill the space requirement for the compound **2**, average distance between molecules along c axis is *c.a.* 8 Å. These results indicate that compounds **1** and **2** take more bulky or twisted conformation in the columnar phases (Fig. 6).

On the other hand, compound **3** forms a hexagonal columnar phase that has 2 molecules per columnar segment (Figs. 5, 6). The fan-shaped oligoglutamate **4**

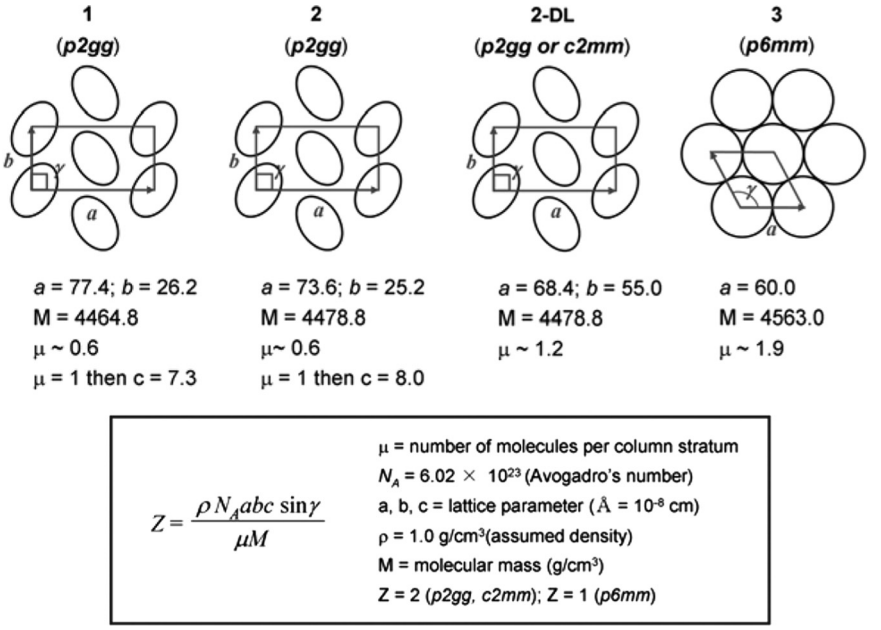

Figure 5. XRD analysis for **1-3** based on Z value equation.

also forms a hexagonal columnar phase, but the column diameter is much smaller than that of **3**. It is considered that the columnar assemblies of **4** are formed by nanoscale segregation between peptide moieties put inside of the columns and alkyl periphery [12]. However, introduction of alkyl spacers between two molecules of **4** requires another segregation between peptide moieties and alkyl spacers. For compound **3**, the spacer is long enough to take flexible conformations and have four of the fan-shaped units per stratum volume V, which stack to form columnar structures.

Homo- and Hetero-Chiral Dimers of Oligopeptides Derivatives

The CD spectra of the LC thin film samples of **2** and **2-DL** were obtained to study the effect of molecular chirality to the LC structures. Clear differences are observed

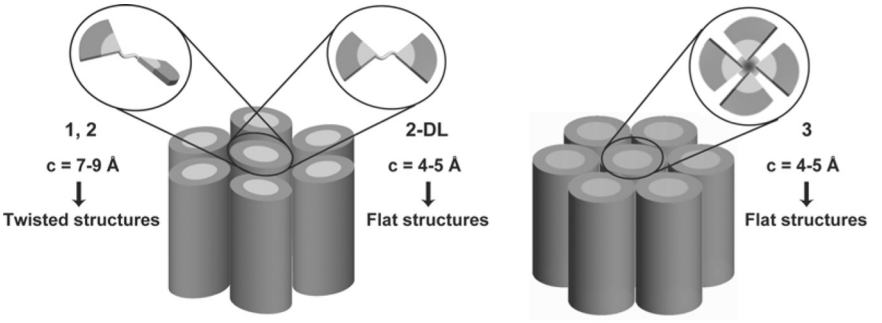

Figure 6. Schematic illustration of compounds **1-3** forming columnar phases.

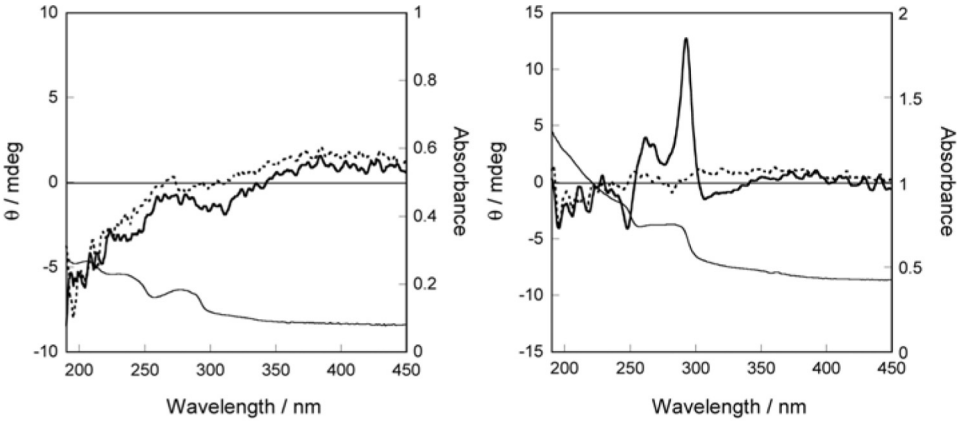

Figure 7. CD and UV-Vis spectra of **2** (a) and **2-DL** (b). Thick solid lines: CD spectra measured in the columnar LC phases (at 90°C); dotted lines: CD spectra measured in the isotropic liquid states, at 150°C for **2** and at 130°C for **2-DL**; thin solid lines: UV-Vis spectra measured at room temperature.

for the spectra obtained in the columnar LC phases (Fig. 7). The CD spectrum for the homochiral dimer **2** keeps almost as silent as that observed for the isotropic state (Fig. 7a). On the other hand, positive CD bands are induced for heterochiral dimer **2-DL** (Fig. 7b). Transfer of molecular chirality requires helical arrangement of the molecules fixed by intermolecular interactions such as hydrogen bonds [14,15]. According to the X-ray results, **2-DL** stacks straightforward keeping flat molecular shape, but compound **2** should take twisted arrangement which may be stabilized by combination of both intra- and intermolecular hydrogen bonds (Table 1).

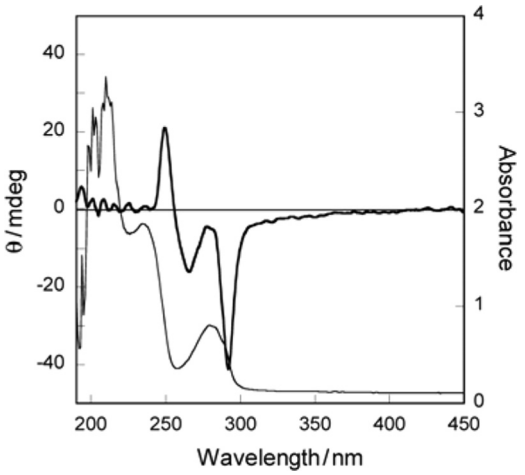

Figure 8. CD and UV-Vis spectra of compound **3**. Thick solid line: CD spectrum measured in the columnar phase at 90°C; thin solid line: UV-Vis spectrum measured at room temperature.

Considering CD results, molecular chirality is reflected in the columnar assemblies of flat stacked structures that are stabilized by intermolecular hydrogen-bonded arrays in parallel to columnar axes. CD effect is also observed for the LC film of compound **3** that takes flat conformation in the columnar phase (Fig. 8). IR results show that amide hydrogen bonds are equally working for the compounds **1**-**3**. One possible explanation is that hydrogen bonds between oligopeptide moieties in **2** contribute more to fix the molecules to arrange into columnar assemblies but do not work much for the transfer of molecular chirality.

Conclusion

We developed thermotropic LC dimers of oligopeptides. The flexible alkyl spacers restrict motion of the fan-shaped oligopeptide units, resulting in the formation of columnar phases with various morphologies and LC temperature ranges. Self-assembly of the LC oligopeptides is initially triggered by nanoscale segregation between peptide moieties and lipophilic segments, then the hydrogen bonds in the peptide parts contribute in different ways to the stabilization of the resulting structures and to transfer molecular chirality, as if polypeptides in water form three-dimensional protein structures via hydrophobic interactions with the aid of hydrogen bonds. These oligopeptide liquid crystals may be a new class of supramolecular materials that are useful in bio-related fields.

References

[1] Special issue on Liquid Crystals (ed. Goodby, J. W.) (2007). *Chem. Soc. Rev.*, *36*, 1845.
[2] Thematic issue on Liquid crystals beyond display applications (ed. Tschierske, C.) (2008). *J. Mater. Chem.*, *18*, 2869.
[3] Kato, T., Mizoshita, N., & Kishimoto, K. (2006). *Angew. Chem. Int. Ed.*, *45*, 38.
[4] Kato, T. (2002). *Science*, *295*, 2414.
[5] Yoshizawa, A. (2008). *J. Mater. Chem.*, *18*, 2877.
[6] Takezoe, H., Kishikawa, K., & Gorecka, E. (2006). *J. Mater. Chem.*, *16*, 2412.
[7] Zannoni, C. (2001). *J. Mater. Chem.*, *11*, 2637.
[8] Fazio, D., Mongin, C., Donnio, B., Galerne, Y., Guillon, D., & Bruce, D. W. (2001). *J. Mater. Chem.*, *11*, 2852.
[9] Robinson, C. (1956). *Trans. Faraday Soc.*, *52*, 571.
[10] Watanabe, J., Fukuda, Y., Gehani, R., & Uematsu, I. (1984). *Macromolecules*, *17*, 1004.
[11] Yu, S. M., Conticello, V. P., Zhang, G., Kayser, C., Fournier, M. J., Mason, T. L., & Tirrell, D. A. (1997). *Nature*, *389*, 167.
[12] Nishii, M., Matsuoka, T., Kamikawa, Y., & Kato, T. (2005). *Org. Biomol. Chem.*, *3*, 875.
[13] Kato, T., Matsuoka, T., Nishii, M., Kamikawa, Y., Kanie, K., Nishimura, T., Yashima, Y., & Ujiie, S. (2004). *Angew. Chem. Int. Ed.*, *43*, 1969.
[14] Kamikawa, Y., Nishii, M., & Kato, T. (2004). *Chem. Eur. J.*, *10*, 5942.
[15] Kamikawa, Y. & Kato, T. (2006). *Org. Lett.*, *8*, 2463.
[16] Kamikawa, Y., Nishii, M., & Kato, T. (2005). *Mol. Cryst. Liq. Cryst.*, *435*, 755.
[17] Aggeli, A., Bell, M., Boden, N., Keen, J. N., Knowles, P. F., McLeish, T. C. B., Pitkeathly, M., & Radford, S. E. (1997). *Nature*, *386*, 259.
[18] Hanabusa, K., Tange, J., Taguchi, Y., Koyama, T., & Shirai, H. (1993). *J. Chem. Soc., Chem. Commun.*, 390.
[19] Jiang, H., Guler, M. O., & Stupp, S. I. (2007). *Soft Matter*, *3*, 454.
[20] Kamikawa, Y. & Kato, T. (2007). *Langmuir*, *23*, 274.

[21] Ghadiri, M. R., Granja, J. R., Milligan, R. A., McRee, D. E., & Khazanovich, N. (1993). *Nature*, *366*, 324.
[22] Goodby, J. W., Mehl, G. H., Saez, I. M., Tuffin, R. P., Mackenzie, G., Auzély-Velty, R., Benvegnu, T., & Plusquellec, D. (1998). *Chem. Commun.*, 2057.
[23] Imrie, C. T. & Henderson, P. A. (2007). *Chem. Soc. Rev.*, *36*, 2096.
[24] Griffin, A. C. & Britt, T. R. (1981). *J. Am. Chem. Soc.*, *103*, 4957.
[25] Lehmann, M., Jahr, M., & Gutmann, G. (2008). *J. Mater. Chem.*, *18*, 2995.
[26] Maringa, N., Lenoble, J., Donnio, B., Guillon, D., & Deschenaux, R. (2008). *J. Mater. Chem.*, *18*, 1524.
[27] Ohtake, T., Ogasawara, M., Ito-Akita, K., Nishina, N., Ujiie, S., Ohno, H., & Kato, T. (2000). *Chem. Mater.*, *12*, 782.
[28] Heinrich, B., Praefcke, K., & Guillon, D. (1997). *J. Mater. Chem.*, *7*, 1363.
[29] Kato, T., Shimizu, Y., Takatoh, K., Yamamoto, J., & Yoshizawa, A. Eds. (2000). *Ekisyo Binran*. (Handbook of Liquid Crystals), Maruzen (in Japanese).