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Odd–Even Effect in Liquid Crystal Tetramers

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A new series of liquid crystal tetramers, which contained four biphenyl groups joined by three flexible spacers, was prepared. The tetramers showed nematic and/or smectic phases. The melting points, the nematic-isotropic transition temperatures, and the entropy changes associated with the nematic–isotropic transition showed a remarkable odd–even effect as the length of the spacers was varied, in which the even members exhibited higher values. The transition properties of the liquid crystal tetramers were compared with those of liquid crystal dimers and trimers, which consist of two and three biphenyl groups.

Keywords: biphenyl; flexible spacer; liquid crystal tetramer; odd-even effect; transition property

INTRODUCTION

Emsley et al. [1] reported the unusual transition properties of liquid crystal dimers containing two 4-cyanobiphenyl groups, BCBOn. Furthermore, the transition properties of many liquid crystal dimers and trimers, which contain two or three mesogenic units, have been studied by many groups of workers [2–5]. In addition, some kinds of liquid crystal tetramers, which are defined as molecules containing four mesogenic units joined by three flexible spacers, have been prepared [6–12]. These compounds exhibit a remarkable odd–even effect in their transition properties, depending on the length and parity of the flexible spacers [1–12]. Liquid crystal dimers, trimers, and tetramers are also of interest as models for main chain liquid crystal polymers [13].

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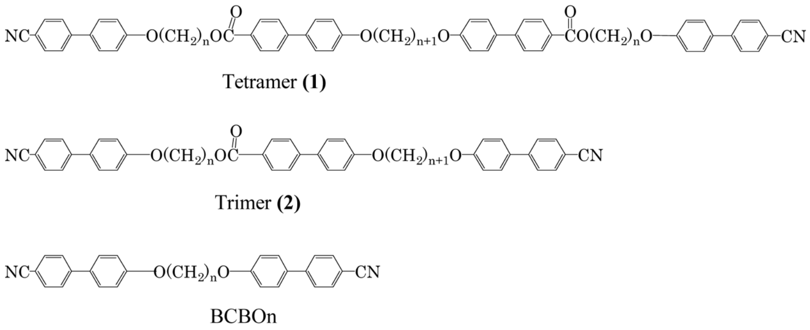


Tetramer **(1)**

Trimer **(2)**

BCBOn

FIGURE 1 Structures of tetramer **(1)**, trimer **(2)**, and BCBOn.

Previously, we reported on the synthesis of liquid crystal trimers **(2)** containing three biphenyl groups [14]. In this article, we report the synthesis and characterization of new liquid crystal tetramers **(1)** containing four biphenyl groups as the mesogenic units. The transition properties of **1** were compared with those of related liquid crystal dimers and trimers containing two and three biphenyl groups, such as BCBOn and trimers **(2)** (Fig. 1).

EXPERIMENTAL

Elemental analyses were performed at the Analytical Center of Kyoto University. ^{1}H-NMR spectra (400 MHz) were obtained with a JEOL GSX 400 spectrometer. The chemical shifts (δ-values) were measured in parts per million (ppm) down-field from tetramethylsilane as an internal reference. IR spectra were recorded with a JASCO FT/IR-420 spectrometer. Measurements in $CDCl_3$ were made with a 0.1-mm KBr cell. Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60. Polarizing microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Linkam LK-600PH).

α,ω-Bis[4-[ω-(4-cyanobiphenyl-4′-yloxy)alkyloxycarbonyl]biphenyl-4′-yloxy]alkane (1)

The preparation of ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-hydroxy-4-biophenylcarboxylate **(3)** has been reported [14]. A mixture of **3** (1.0 mmol) and α,ω-dibromoalkane (0.7 mmol) in N,N-dimethylformamide (40 ml) in the presence of K_2CO_3 (2.0 mmol) was stirred for 24 h at room temperature. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. An elution with

TABLE 1 Elemental Analyses and Yields of Tetramers **(1)**

n	%[a]	Calculated	Found
4	60	$C_{65}H_{58}N_2O_8$: C, 78.45, H, 5.87; N, 2.81%	C, 78.41, H, 5.88; N, 2.76%
5	58	$C_{68}H_{64}N_2O_8$: C, 78.74, H, 6.22; N, 2.70%	C, 78.72, H, 6.12; N, 2.70%
6	58	$C_{71}H_{70}N_2O_8$: C, 79.01, H, 6.54; N, 2.60%	C, 78.78, H, 6.48; N, 2.79%
7	55	$C_{74}H_{76}N_2O_8$: C, 79.26, H, 6.83; N, 2.50%	C, 79.03, H, 6.83; N, 2.49%
8	55	$C_{77}H_{82}N_2O_8$: C, 79.49, H, 7.10; N, 2.41%	C, 79.53, H, 7.12; N, 2.37%
9	55	$C_{80}H_{88}N_2O_8$: C, 79.70, H, 7.36; N, 2.32%	C, 79.82, H, 7.20; N, 2.82%
10	52	$C_{83}H_{94}N_2O_8$: C, 79.90, H, 7.59; N, 2.25%	C, 79.93, H, 7.59; N, 2.47%
11	50	$C_{86}H_{100}N_2O_8$: C, 80.09, H, 7.81; N, 2.17%	C, 79.60, H, 7.77; N, 2.13%

[a] Yield based on the amount of **3** used.

chloroform or a mixture of chloroform and methanol (9:1) gave liquid crystal tetramers **(1)**. The yields, based on the amount of **3** used, are shown in Table 1.

RESULTS AND DISCUSSION

Liquid crystal tetramers **(1)** were prepared according to the procedure shown in Fig. 2. All the structures of **1** were confirmed on the basis of elemental analyses (Table 1), the IR spectral data (Table 2), and ^{1}H-NMR spectral data (Table 3). The IR spectral data of **1** showed the presence of a cyano group at 2227 cm^{-1} and an ester group at ca. 1711 cm^{-1}. The ^{1}H-NMR spectral data of **1** were similar to those of liquid crystal trimers **(2)** [14], but the integration ratio of the absorptions at δ 4.34–4.44 (CH_2COO) to δ 4.00–4.11 (CH_2O) was 1:2.

The thermal mesomorphic phases of tetramers **(1)** were investigated by differential scanning calorimetry (DSC) and polarizing microscopy. Each of the tetramers, except **1** (n = 4), exhibited enantiotropic

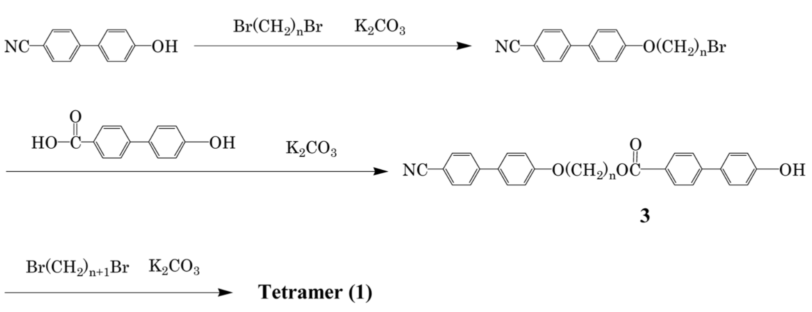


FIGURE 2 Synthesis of liquid crystal tetramers **(1)**.

TABLE 2 IR Spectral Data of Tetramers **(1)**

n	cm^{-1}/CDCl$_3$
4	2951, 2873, 2227, 1712, 1606, 1525, 1495, 1471, 1277, 1248, 1182, 1115
5	2943, 2862, 2227, 1712, 1606, 1523, 1495, 1471, 1279, 1248, 1182, 1115
6	2943, 2862, 2227, 1711, 1605, 1525, 1495, 1470, 1279, 1248, 1182, 1115
7	2937, 2860, 2227, 1711, 1606, 1523, 1495, 1471, 1279, 1248, 1180, 1115
8	2937, 2858, 2227, 1711, 1606, 1523, 1495, 1471, 1281, 1248, 1182, 1115
9	2933, 2858, 2227, 1710, 1606, 1523, 1495, 1471, 1279, 1248, 1182, 1115
10	2931, 2856, 2227, 1710, 1606, 1523, 1495, 1471, 1279, 1248, 1182, 1115
11	2931, 2856, 2227, 1712, 1605, 1525, 1495, 1470, 1279, 1248, 1182, 1115

TABLE 3 ^{1}H-NMR Spectral Data of Tetramers **(1)**

n	δ/CDCl$_3$
4	8.05 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 7.00 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.44 (broad, 4H), 4.11 (broad, 4H), 4.06 (t, 4H, J = 7 Hz), 2.01 (broad, 8H), 1.92 (quintet, 4H, J = 7 Hz), 1.72 (quintet, 2H, J = 7 Hz).
5	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.39 (t, 4H, J = 6 Hz), 4.05 (t, 4H, J = 6 Hz), 4.04 (t, 4H, J = 6 Hz), 1.8–1.9 (m, 12H), 1.6–1.8 (m, 8H).
6	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.36 (t, 4H, J = 6 Hz), 4.03 (t, 4H, J = 6 Hz), 4.02 (t, 4H, J = 6 Hz), 1.8–1.9 (m, 12H), 1.4–1.6 (m, 14H).
7	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.35 (t, 4H, J = 6 Hz), 4.01 (t, 8H, J = 6 Hz), 1.75–1.85 (m, 12H), 1.4–1.6 (m, 20H).
8	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.34 (t, 4H, J = 6 Hz), 4.00 (t, 8H, J = 6 Hz), 1.75–1.85 (m, 12H), 1.35–1.6 (m, 26H).
9	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.33 (t, 4H, J = 6 Hz), 4.00 (t, 8H, J = 6 Hz), 1.75–1.85 (m, 12H), 1.35–1.6 (m, 32H).
10	8.07 (d, 4H, J = 8 Hz), 7.68 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.59 (d, 4H, J = 8 Hz), 7.53 (d, 4H, J = 8 Hz), 7.52 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.33 (t, 4H, J = 6 Hz), 4.00 (t, 8H, J = 6 Hz), 1.75–1.85 (m, 12H), 1.3–1.6 (m, 38H).
11	8.07 (d, 4H, J = 8 Hz), 7.69 (d, 4H, J = 8 Hz), 7.63 (d, 4H, J = 8 Hz), 7.61 (d, 4H, J = 8 Hz), 7.55 (d, 4H, J = 8 Hz), 7.51 (d, 4H, J = 8 Hz), 6.99 (d, 4H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 4.33 (t, 4H, J = 6 Hz), 4.00 (t, 8H, J = 6 Hz), 1.75–1.85 (m, 12H), 1.3–1.6 (m, 44H).

liquid crystalline behavior. The tetramers exhibited nematic and/or smectic liquid crystalline properties. Tetramers **(1)** (n = 4 and 5) showed only the nematic phase (Schlieren texture) and **1** (n = 11) displayed only the smectic A phase (focal-conic texture). Tetramers **(1)** (n = 6–10) manifested both the smectic and nematic phases. Figure 3 shows the polarizing microscopic images of **1** (n = 8, 9, and 10). Figures 3A, B shows the optical textures of the smectic phase at 146°C and the nematic phase at 165°C upon the second heating for **1** (n = 8), respectively. The smectic phase had a focal-conic texture, which was characteristic of smectic A. Tetramer **(1)** (n = 9) also

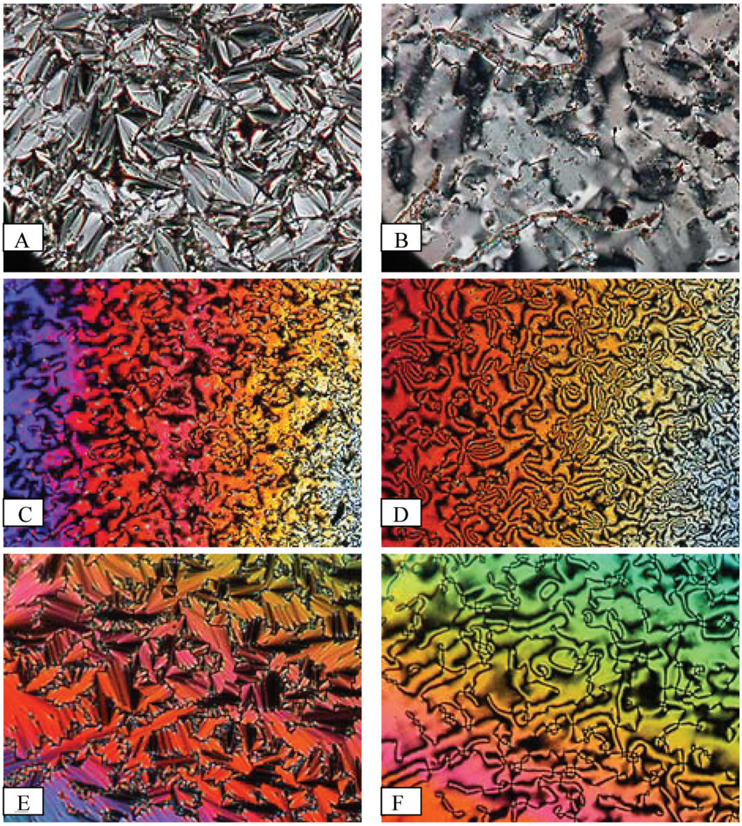


FIGURE 3 Representative polarizing microscopic images of tetramers **(1)**, obtained upon the second heating. (A): Tetramer **(1)** (n = 8), SmA phase at 146°C; (B): Tetramer **(1)** (n = 8), N phase at 165°C; (C): Tetramer **(1)** (n = 9), SmC phase at 170°C; (D): Tetramer **(1)** (n = 9), N phase at 180°C; (E): Tetramer **(1)** (n = 10), SmA phase at 140°C; (F): Tetramer **(1)** (n = 10), N phase at 155°C.

manifested both the smectic and nematic phases, but the smectic phase was smectic C (Schlieren texture), not smectic A. Figures 3C, D shows the Schlieren textures of the tilted smectic phase at 170°C and the nematic phase at 180°C upon the second heating, respectively. Figures 3E, F shows the optical textures of the smectic A phase (focal-conic texture) at 140°C and the nematic phase at 155°C upon the second heating for **1** ($n = 10$), respectively. The transition properties of tetramers **(1)** are summarized in Table 4.

Tetramers **(1)** contain two kinds of flexible spacers, such as the $O(CH_2)_{n+1}O$ and $COO(CH_2)_nO$ groups, but the number (k) of atoms in the two flexible spacers is equivalent, i.e., $k = n + 3$. Figure 4 shows the occurrence of the liquid crystal phases of tetramers **(1)**. As we varied the number (k) of atoms in the flexible spacers, the nematic–isotropic transition temperature exhibited an odd–even effect, in which the even numbers exhibited higher values. Figure 4 also indicates an odd–even behavior of the melting point and smectic-nematic transition temperature.

The transition properties of tetramers **(1)** were compared with those of trimers **(2)** and dimers, BCBOn. Figure 5 indicates the presence of an odd–even effect of the melting point and the nematic–isotropic transition temperature on the number (k) of atoms in the flexible spacers for **1**, **2**, and BCBOn, but the transition temperature of **1** ($k = 11-14$) seems to deviate somewhat from the expected values. This deviation may come from the formation of the smectic phase of **1**, because **2** and BCBOn exhibit only the nematic phase but no smectic

TABLE 4 Transition Properties of Tetramers **(1)**

n	T_M/°C	T_{SN}/°C	T_{SI}/°C	T_{NI}/°C	$\Delta S_M/R$	$\Delta S_{SN}/R$	$\Delta S_{SI}/R$	$\Delta S_{NI}/R$
4	193			(174)	14.2			(0.44)
5	242			251	13.7			3.57
6	160	(153)		182	13.5	(1.60)		0.57
7	214	(194)		224	12.8	(0.40)		3.65
8	143	160		175	12.3	1.78		0.95
9	151	173[a]		188	14.2	0.82[a]		3.79
10	138	150		167	17.2	1.02		1.72
11	178		190		16.9		6.37	

T_M: melting point.
T_{SN}: smectic A-nematic transition temperature except for $n = 9$.
T_{SI}: smectic A-isotropic transition temperature.
T_{NI}: nematic–isotropic transition temperature.
( ): upon cooling.
[a] T_{SN}: smectic C-nematic transition temperature.

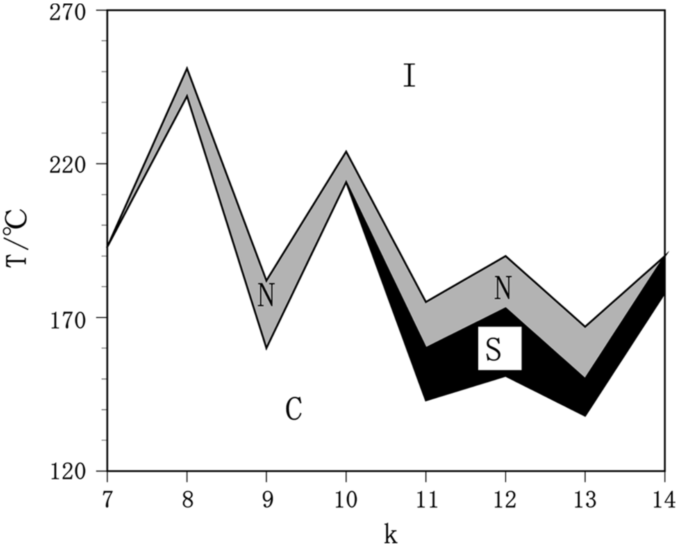
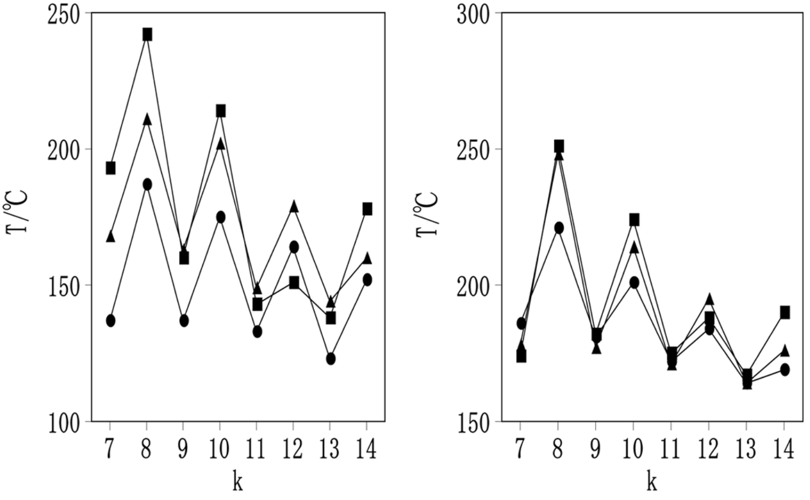


FIGURE 4 Dependence of liquid crystal phase on the number (k) of atoms in the flexible spacers for tetramers **(1)**; k = n + 3; C: crystal; N: nematic; S: smectic; I: isotropic liquid.



(A) (B)

FIGURE 5 Comparison of transition temperatures of tetramer **(1)**, trimer **(2)**, and BCBOn; (A) Melting point; (B) Nematic–isotropic or smectic–isotropic transition temperature; k = n + 3 for tetramer **(1)** and trimer **(2)**; k = n + 2 for BCBOn; ■: Tetramer **(1)**; ▲: Trimer **(2)**; ●: BCBOn.

phase. Furthermore, Fig. 5B shows that the nematic–isotropic transition temperature is significantly dependent on the number (k) of atoms in the flexible spacers for even-membered tetramers, trimers, and dimers, compared with odd-membered tetramers, trimers, and dimers.

Although the entropy changes associated with the melting points of tetramers **(1)**, trimers **(2)**, and BCBOn did not result in an odd–even effect on the number of atoms in the flexible spacers (Fig. 6A), these compounds evinced an odd–even effect with the entropy changes associated with the nematic–isotropic transition (Fig. 6B). The entropy changes associated with the nematic–isotropic transition were dependent on the number (k) of atoms in the flexible spacers for odd-membered tetramers, trimers, and dimers. The values of the entropy change of the odd-membered tetramers resembled those of the corresponding odd-membered trimers and dimers. On the other hand, as for the even-membered tetramers, trimers, and dimers, the values of the entropy changes were only slightly affected by the number (k) of atoms in the flexible spacers. It can be seen from Fig. 6B that the average value of the even-membered tetramers (k = 8, 10, and 12) is

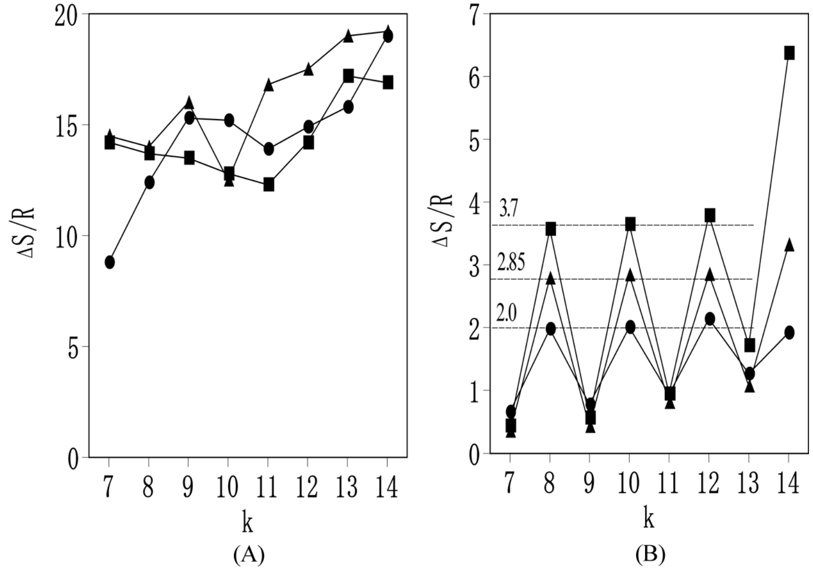


FIGURE 6 Comparison of entropy change associated with phase transition of tetramer **(1)**, trimer **(2)**, and BCBOn; (A) Melting point; (B) Nematic–isotropic or smectic–isotropic transition; k = n + 3 for tetramer **1** and **2**; k = n + 2 for BCBOn; ■: Tetramer **(1)**; ▲: Trimer **(2)**; ●: BCBOn.

ca. 3.7, the average value of the even-membered trimers (k = 8, 10, and 12) is ca. 2.85, and the average value of even-membered dimers (k = 8, 10, and 12) is ca. 2.0. Imrie et al. [15–17] have already reported similar thermodynamic behavior of liquid crystal dimers and trimers, which was explained on the basis of the molecular shapes of the all-*trans*-conformation of the compounds containing odd- and even-membered flexible spacers. The present results substantiate the regular array seen in the thermodynamic behavior of dimers, trimers, and tetramers, which consist of two, three, and four biphenyl groups as the mesogenic units.

CONCLUSION

A new series of liquid crystal tetramers, which contained four biphenyl groups joined by three flexible spacers, was prepared. The tetramers exhibited nematic and/or smectic phases. The melting points, the nematic–isotropic transition temperatures, and the entropy changes associated with the nematic–isotropic transition showed an odd–even effect as the number of atoms in the spacers was varied, in which the even members exhibited higher values. The transition properties of the tetramers were compared with those of related liquid crystal dimers and trimers containing two and three biphenyl groups. The entropy changes associated with the nematic–isotropic transition were only slightly affected by the number of atoms in the flexible spacers for even-membered tetramers, trimers, and dimers. The values of the entropy changes of the even-membered tetramers, the even-membered trimers, and the even-membered dimers regularly decreased, in that order.

REFERENCES

[1] Emsley, J. E., Luckhurst, G. R., Shilstone, G. N., & Sage, I. (1984). *Mol. Cryst. Liq. Cryst. Lett.*, *102*, 223.

[2] Imrie, C. T., & Luckhurst, G. R. (1998). Liquid crystal dimers and oligomers. In: *Handbook of Liquid Crystals*. Demus, D., Goodby, J., Gray, W. G., Spiess, H. W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 2B, Chapter X, p. 801.

[3] Imrie, C. T. (1999). *Struct. Bonding*, *95*, 149.

[4] Imrie, C. T., & Henderson, P. A. (2002). *Curr. Opin. Colloid Interface Sci.*, *7*, 298.

[5] Abe, A., Furuya, H., Zhou, Z. P., Hiejima, T., & Kobayashi, Y. (2005). *Adv. Polym. Sci.*, *181*, 121.

[6] Griffin, A. C., Sullivan, S. L., & Hughes, W. E. (1989). *Liq. Cryst.*, *4*, 677.

[7] Imrie, C. T., Stewart, D., Remy, C., Christie, D. W., Hamley, I. W., & Harding, R. (1999). *J. Mater. Chem.*, *9*, 2321.

[8] Henderson, P. A., Inkster, R. T., Seddon, J. M., & Imrie, C. T. (2001). *J. Mater. Chem.*, *11*, 2722.

[9] Yelamaggad, C. V., Nagamani, S. A., Hiremath, U. S., Rao, D. S. S., & Prasad, S. K. (2002). *Liq. Cryst.*, *29*, 231.
[10] Sasanuma, Y., Ono, T., Kuroda, Y., Miyazaki, E., Hikino, K., Arou, J., Nakata, K., Inaba, H., Tozaki, K., Hayashi, H., & Yamaguchi, K. (2004). *J. Phys. Chem. B*, *108*, 13163.
[11] Henderson, P. A., & Imrie, C. T. (2005). *Macromolecules*, *38*, 3307.
[12] Henderson, P. A., & Imrie, C. T. (2005). *Liq. Cryst.*, *32*, 1531.
[13] Chiellini, E., & Laus, M. (1998). Main chain liquid crystalline semiflexible polymers. In: *Handbook of Liquid Crystals*. Demus, D., Goodby, J., Gray, W. G., Spiess, H. W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 3, Chapter II, p. 93.
[14] Itahara, T., & Tamura, H. (2007). *Mol. Cryst. Liq. Cryst.*, *474*, 17.
[15] Imrie, C. T., & Luckhurst, G. R. (1998). *J. Mater. Chem.*, *8*, 1339.
[16] Henderson, P. A., Cook, A. G., & Imrie, C. T. (2004). *Liq. Cryst.*, *31*, 1427.
[17] Imrie, C. T., & Henderson, P. A. (2005). *Liq. Cryst.*, *32*, 673.