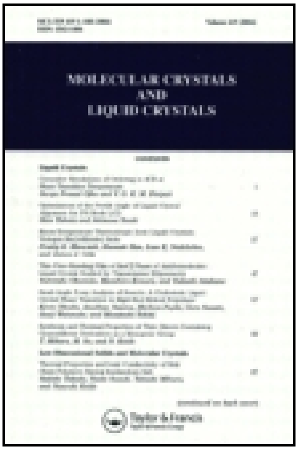

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Vinyl-Substituted Liquid Crystal Dimers

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Vinyl-Substituted Liquid Crystal Dimers

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A series of vinyl-substituted liquid crystal dimers, ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-(4-pentenyloxy)-4-biphenylcarboxylates, was prepared. The compounds exhibited nematic and smectic liquid crystalline behavior depending on the chain length of the flexible spacer. The nematic-isotropic and smectic-isotropic transition temperatures and the entropy changes associated with the transitions showed odd–even effects as the number of atoms in the flexible spacer was varied, in which the even members exhibited higher values. The liquid crystalline properties of the compounds were compared with those of related known liquid crystal dimers and trimers.

Keywords: liquid crystal dimer; nematic; odd–even effect; smectic; vinyl

INTRODUCTION

Liquid crystalline compounds with attached alkenyl groups (mesogenic olefins) are of importance as monomers for side chain liquid crystal polymers. On the other hand, liquid crystal dimers, which are defined as molecules containing two mesogenic units joined by one flexible spacer, have been extensively studied as model compounds for main chain liquid crystal polymers [1–4]. The liquid crystal dimers, such as BCBOn [5], exhibit an interesting odd–even effect of liquid crystalline properties, depending on the number of atoms in the flexible spacer [1–5]. The odd–even effect has been explained on the basis of the molecular shapes of all-*trans*-conformation of the compounds containing odd and even membered flexible spacers [1–4]. We are very interested in side chain liquid crystal polymers containing liquid crystal dimers, in connection with potential functional materials, such as liquid crystal elastomers [6]. We also previously reported on the synthesis of liquid

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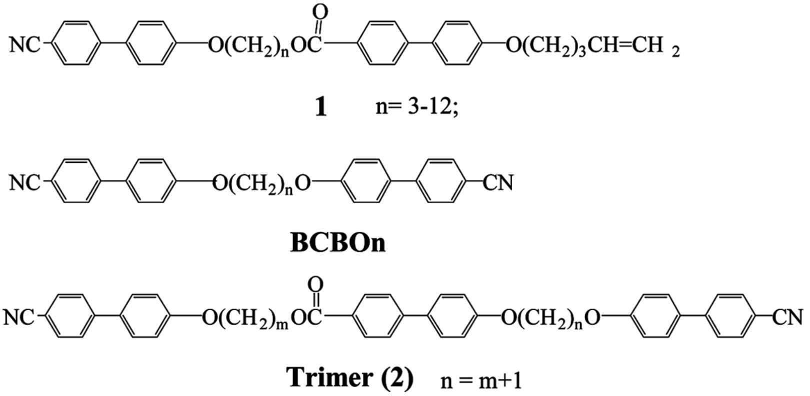

FIGURE 1 Structures of compound **(1)**, BCBOn, and trimer **(2)**.

crystal trimers **(2)** from α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkanes **(3)** and ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-hydroxy-4-biophenylcarboxylates **(4)** [7]. The present article reports on the synthesis of a new series of vinyl-substituted liquid crystal dimers **(1)** from **4** and 5-bromo-1-pentene (Fig. 1). The liquid crystalline properties of **1** were compared with those of BCBOn and **2**.

EXPERIMENTAL

Elemental analyses were performed at the Analytical Center of Kyoto University. ^{1}H-NMR spectra (400 M Hz) 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. Infrared (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).

ω-(4-Cyanobiphenyl-4′-yloxy)alkyl 4′-(4-pentenyloxy)-4-biphenylcarboxylate (1)

A mixture of ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-hydroxy-4-biophenylcarboxylate **(4)** [7] (1.0 mmol) and 5-bromo-1-pentene (1.2 mmol) in N,N-dimethylformamide (40 ml) in the presence of K_2CO_3 (1.0 mmol) was stirred for 24 h at room temperature. The reaction

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

n	Yield[a]	Calculated (%)	Found (%)
3	71	$C_{34}H_{31}NO_4$: C:78.89, H, 6.04; N, 2.71	C, 79.08; H, 6.11; N, 2.65
4	70	$C_{35}H_{33}NO_4$: C:79.07, H, 6.26; N, 2.63	C, 79.19; H, 6.31; N, 2.55.
5	73	$C_{36}H_{35}NO_4$: C:79.24, H, 6.46; N, 2.57	C, 79.33; H, 6.47; N, 2.55.
6	75	$C_{37}H_{37}NO_4$: C:79.40, H, 6.66; N, 2.50	C, 79.31; H, 6.56; N, 2.56.
7	70	$C_{38}H_{39}NO_4$: C:79.55, H, 6.85; N, 2.44	C, 79.56; H, 7.01; N, 2.43.
8	74	$C_{39}H_{41}NO_4$: C, 79.70; H, 7.03; N, 2.38	C, 79.85; H, 7.15; N, 2.38.
9	71	$C_{40}H_{43}NO_4$: C:79.84, H, 7.20; N, 2.33	C, 80.04; H, 7.19; N, 2.35.
10	76	$C_{41}H_{45}NO_4$: C, 79.97; H, 7.37; N, 2.27	C, 80.00; H, 7.43; N, 2.29.
11	72	$C_{42}H_{47}NO_4$: C, 80.08; H, 7.52; N, 2.22	C, 80.03; H, 7.61; N, 2.22.
12	73	$C_{43}H_{49}NO_4$: C, 80.21; H, 7.67; N, 2.18	C, 80.16; H, 7.70; N, 2.17.

[a] Yield based on the amount of **4** used.

mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of a mixture of chloroform and hexane (2:1) gave **1**. The yields of **1** (n = 3–12) are shown in Table 1.

RESULTS AND DISCUSSION

Compounds **(1)** were synthesized according to the procedure shown in Figure 2. Previously, we reported on the synthesis of liquid crystal trimers **(2)** from **3** and **4** [7]. The reaction of **4** with 5-bromo-1-pentene in N,N-dimethylformamide in the presence of K_2CO_3 gave **1** in 70–76% yields. The elemental analyses of **1** (n = 3–12) are shown in Table 1. The IR spectral data of **1** (Table 2) showed the presence of a cyano group at 2227 cm^{-1}, an ester group at ca. 1711 cm^{-1}, and a vinyl group at ca. 1653 cm^{-1} (weak bands). The ^{1}H-NMR spectral data of **1** are

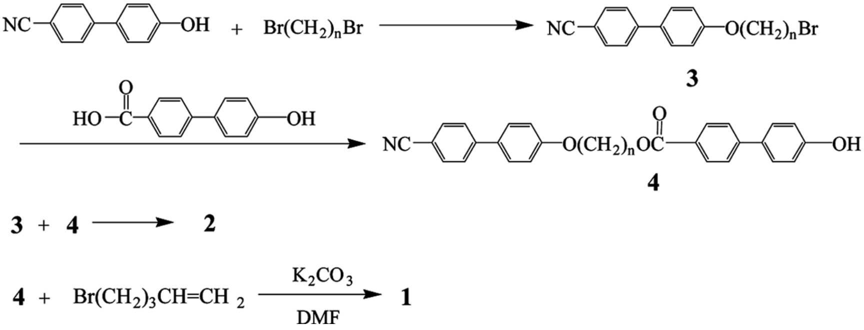

FIGURE 2 Synthesis of compounds **(1)**.

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

n	$cm^{-1}/CDCl_3$
3	2949, 2879, 2227, 1714, 1653, 1606, 1525, 1496, 1400, 1279, 1248, 1182, 1115
4	2952, 2875, 2227, 1712, 1653, 1606, 1525, 1497, 1389, 1277, 1248, 1182, 1115
5	2948, 2873, 2227, 1712, 1653, 1606, 1524, 1495, 1394, 1279, 1248, 1182, 1115
6	2939, 2860, 2227, 1711, 1853, 1606, 1523, 1495, 1390, 1279, 1248, 1182, 1115
7	2939, 2858, 2227, 1711, 1653, 1606, 1523, 1496, 1396, 1279, 1247, 1182, 1115
8	2937, 2858, 2227, 1714, 1653, 1606, 1523, 1496, 1389, 1279, 1248, 1182, 1115
9	2937, 2858, 2227, 1711, 1655, 1606, 1525, 1495, 1390, 1279, 1248, 1182, 1115
10	2931, 2858, 2227, 1711, 1653, 1606, 1523, 1495, 1390, 1279, 1248, 1182, 1115
11	2931, 2856, 2227, 1709, 1653, 1606, 1523, 1495, 1389, 1279, 1248, 1182, 1115
12	2929, 2856, 2227, 1711, 1651, 1606, 1525, 1495, 1390, 1279, 1248, 1182, 1115

summarized in Table 3. The absorptions of **1** at δ 5.88, 5.08, and 5.02 were assigned to the vinyl group.

The thermal mesomorphic phases of **1** (n = 3–12) were analyzed by means of DSC and polarizing microscopy. The transition properties are summarized in Table 4. Compounds **(1)** (except for n = 4) exhibited enantiotropic liquid crystalline behavior, although **1** (n = 4) exhibited the nematic phase only upon cooling. Compounds **(1)** (n = 3–6) displayed only nematic liquid crystalline behavior, while **1** (n = 7, 8, 10, and 12) manifested both the nematic and smectic phases and **1** (n = 9 and 11) showed only the smectic phase. Figure 3 shows the representative polarizing microscopic images of **1**. The nematic phase of **1** (n = 3) had a Schlieren optical texture (Fig. 3A). The smectic phase of **1** (n = 9) (Fig. 3B) had a focal-conic fan texture, which was characteristic of smectic A. It is known that BCBOn [5] and **2** [7] exhibit only nematic liquid crystalline behavior. Therefore, the formation of the smectic phase of **1** may result from the existence of the vinyl group.

The polarizing microscopy observations substantiated the formation of the nematic and smectic A phases of **1** (n = 7). Figures 3c and d shows the optical textures of the smectic A phase at 136°C and the nematic phase at 155°C upon heating, respectively. However, it was not easy to find the SmA-N transition peak in the DSC thermogram because the peak was very small. Figure 4 shows the enlarged DSC thermogram of **1** (n = 7). In contrast to the very small peak of the SmA-N transition of **1** (n = 7), the DSC thermograms of **1** (n = 8, 10, and 12) showed distinct peaks of the SmA-N transition, although the smectic phase of **1** (n = 8) was found only upon cooling. Figures 3e, f shows the optical textures of the smectic A phase at 105°C and the nematic phase at 111°C for **1** (n = 10) upon heating, respectively. The difference in the SmA-N transitions between **1** (n = 7) and

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

n	δ/CDCl$_3$
3	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 7.00(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.56(t,2H, J = 6.5 Hz), 4.21(t, 2H, J = 6.5 Hz), 4.03(t, 2H, J = 6.5 Hz), 2.31(quintet, 2H, J = 6.5 Hz), 2.27(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz).
4	8.06(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.99(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.35(broad t, 2H), 4.11(broad t, 2H), 4.03(t, 2H, J = 6.5 Hz), 2.27(q, 2H, J = 6.5 Hz), 2.01(broad m, 4H), 1.92(quintet, 2H, J = 6.5 Hz).
5	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.38(t, 2H, J = 6.5 Hz), 4.05(t, 2H, J = 6.5 Hz), 4.03(t, 2H, J = 6.5 Hz), 2.27(q, 2H, J = 6.5 Hz), 1.96-1.85(m, 6H), 1.68(quintet, 2H).
6	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.62(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.36(t, 2H, J = 6.5 Hz), 4.03(t, 2H, J = 6.5 Hz), 4.02(t, 2H, J = 6.5 Hz), 2.27(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.5(m, 4H).
7	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.62(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.35(t, 2H, J = 6.5 Hz), 4.02(t, 2H, J = 6.5 Hz), 4.01(t, 2H, J = 6.5 Hz), 2.27(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.4(m, 6H).
8	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.62(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.34(t, 2H, J = 6.5 Hz), 4.02(t, 2H, J = 6.5 Hz), 4.01(t, 2H, J = 6.5 Hz), 2.26(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.4(m, 8H).
9	8.07(d, 2H, J = 8 Hz), 7.68(d, 2H, J = 8 Hz), 7.62(d, 2H, J = 8 Hz), 7.60(d, 2H, J = 8 Hz), 7.54(d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.36(t, 2H, J = 6.5 Hz), 4.03(t, 2H, J = 6.5 Hz), 4.02(t, 2H, J = 6.5 Hz), 2.26(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.3(m, 10H).

(*Continued*)

TABLE 3 Continued

n	δ/$CDCl_3$
10	8.07(d, 2H, J = 8 Hz), 7.69(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.61(d, 2H, J = 8 Hz), 7.55(d, 2H, J = 8 Hz), 7.52(d, 2H, J = 8 Hz), 6.98(d, 2H, J = 8 Hz), 6.97(d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.33(t, 2H, J = 6.5 Hz), 4.02(t, 2H, J = 6.5 Hz), 4.00(t, 2H, J = 6.5 Hz), 2.26(q, 2H, J = 6.5 Hz), 1.91(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.3(m, 12H).
11	8.07(d, 2H, J = 8 Hz), 7.69(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.61(d, 2H, J = 8 Hz), 7.55 (d, 2H, J = 8 Hz), 7.51(d, 2H, J = 8 Hz), 6.99(d, 2H, J = 8 Hz), 6.98 (d, 2H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.33(t, 2H, J = 6.5 Hz), 4.02 (t, 2H, J = 6.5 Hz), 4.00(t, 2H, J = 6.5 Hz), 2.26(q, 2H, J = 6.5 Hz), 1.92(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.3(m, 14H).
12	8.07(d, 2H, J = 8 Hz), 7.69(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.61(d, 2H, J = 8 Hz), 7.55 (d, 2H, J = 8 Hz), 7.52(d, 2H, J = 8 Hz), 6.98(d, 4H, J = 8 Hz), 5.88(m, 1H), 5.08(dd, 1H, J = 16 Hz, J = 2 Hz), 5.02(dd, 1H, J = 12 Hz, J = 2 Hz), 4.33(t, 2H, J = 6.5 Hz), 4.02 (t, 2H, J = 6.5 Hz), 4.00(t, 2H, J = 6.5 Hz), 2.26(q, 2H, J = 6.5 Hz), 1.91(quintet, 2H, J = 6.5 Hz), 1.84-1.74(m, 4H), 1.6-1.3(m, 16H).

1 (n = 8, 10, and 12) may be related to an odd–even effect, depending on the number (n) of methylene units of the polymethylene group of **1**.

Figure 5 shows the dependence of the liquid crystal phases on the number (n) of methylene units of the polymethylene group of **1**. The nematic-isotropic and smectic-isotropic transition temperatures

TABLE 4 Transitional Properties of Compounds **(1)**

n	k	T_M/°C	T_{SN}/°C	T_{SI}/°C	T_{NI}/°C	$\Delta S_M/R$	$\Delta S_{SN}/R$	$\Delta S_{SI}/R$	$\Delta S_{NI}/R$
3	6	157			203	10.58			1.36
4	7	131			(115)	12.92			(0.18)
5	8	125			182	11.06			1.51
6	9	105			118	9.56			0.20
7	10	134	137		164	8.48	0.06		1.72
8	11	108	(100)		119	8.22	(0.46)		0.22
9	12	118		155		10.06		3.19	
10	13	103	110		122	8.94	0.98		0.60
11	14	101		149		9.72		3.27	
12	15	97	112		122	9.35	0.55		0.62

n: the number of methylene units of the polymethylene chain of **1**. k = n + 3: the number of atoms in the flexible spacer of **1**. M: melting point. SN: smectic-nematic transition. SI: smectic-isotropic transition. NI: nematic-isotropic transition. Parentheses indicate monotropic transitions.

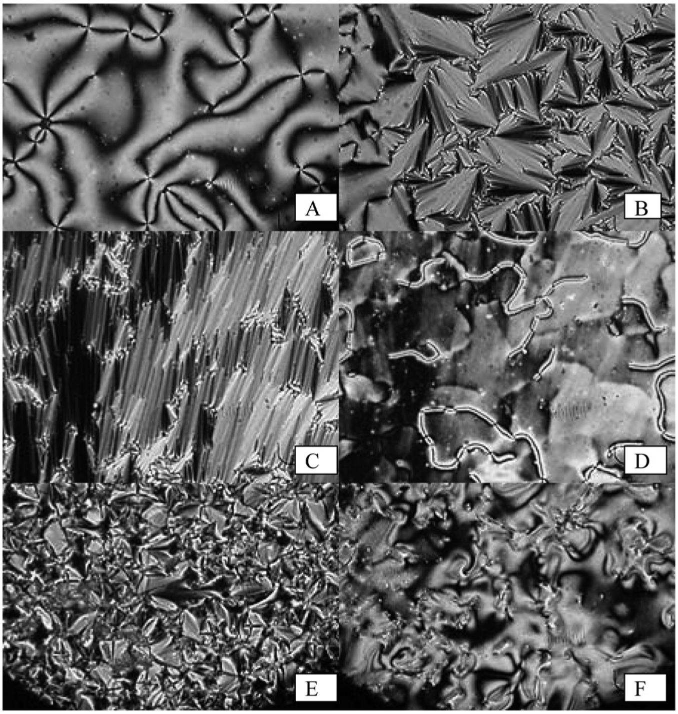

FIGURE 3 Representative polarizing microscopic images of compounds **(1)**. **A**: Compound **(1)** ($n = 3$) at 199°C upon cooling. **B**: Compound **(1)** ($n = 9$) at 151°C upon cooling. **C**: Compound **(1)** ($n = 7$) at 136°C upon heating. **D**: Compound **(1)** ($n = 7$) at 155°C upon heating. **E**: Compound **(1)** ($n = 10$) at 105°C upon heating. **F**: Compound **(1)** ($n = 10$) at 111°C upon heating.

exhibited an odd–even effect as the number (n) of methylene units was varied, in which the odd numbers exhibited higher values. However, the number (k) of atoms in the flexible spacer of **1** is $n + 3$. Therefore, the results indicate that even numbers of atoms in the flexible spacer exhibit higher values, and are consistent with the known odd–even effect of liquid crystal dimers [1–5].

The thermodynamic data of **1** were compared with those of BCBOn [5] and the liquid crystal trimers **(2)** [7]. Figure 6 shows the dependence of the entropy changes associated with the nematic-isotropic and smectic-isotropic transitions ($\Delta S_{NI}/R$ and $\Delta S_{SI}/R$) on the number (k) of atoms in the flexible spacers for **1**, BCBOn, and **2**. In Fig. 6, the abscissa indicates the number (k) of atoms in the flexible spacers of **1**, BCBOn, and **2**. That is to say, k is $n + 3$ for **1**, k is $n + 2$ for BCBOn,

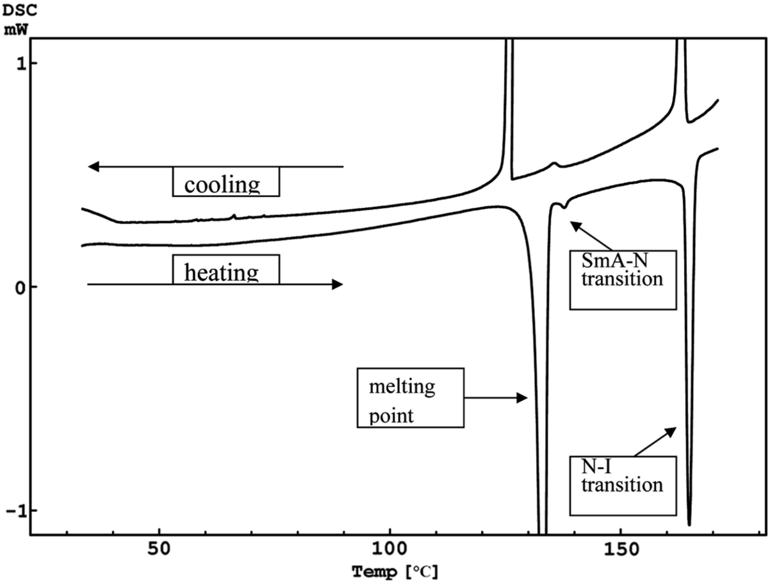

FIGURE 4 DSC thermogram of compound **(1)** (n = 7), obtained upon second heating and cooling at a rate of 5°C/min.

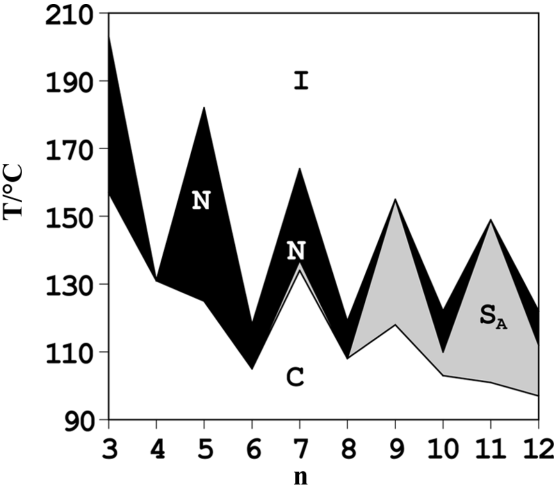

FIGURE 5 Dependence of liquid crystal phases on number (n) of methylene units of polymethylene chain for compounds **(1)** upon heating. C: crystal. N: nematic. S_A: smectic A. I: isotropic liquid. Compound **(1)** (n = 4) showed the nematic phase upon cooling at 115°C. Compound **(1)** (n = 8) showed the smectic A phase upon cooling at 100°C.

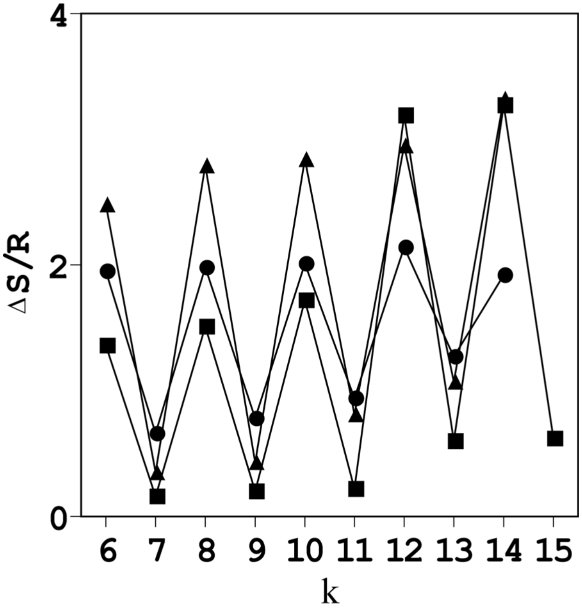

FIGURE 6 Dependence of entropy change associated with nematic-isotropic and smectic-isotropic transitions on number (k) of atoms in flexible spacers for compounds **(1)**, BCBOn, and trimers **(2)**. $k = n + 3$ for **1**, $k = n + 2$ for BCBOn, and $k = n + 2$ for **2**. ■: Nematic-isotropic transition (except for $k = 12$ and 14) and smectic-isotropic transition ($k = 12$ and 14) of **1**. ●: Nematic-isotropic transition of BCBOn. ▲: Nematic-isotropic transition of **2**.

and k is $n + 2$ for **2**. Figure 6 unquestionably shows an odd–even effect of $\Delta S_{NI}/R$ and $\Delta S_{SI}/R$ for **1** as the number of atoms in the flexible spacers is varied, in which the even members exhibit higher values. The odd–even effect of **1** resembles those of BCBOn and **2** very much. However, it can be seen from Fig. 6 that the values of $\Delta S_{NI}/R$ of **1** are clearly lower than those of BCBOn and **2**. The differences between **1** and BCBOn may result from the polarizability and shape of liquid crystal dimers. Furthermore, the values of $\Delta S_{NI}/R$ of **1** are about half those of **2**, although Imrie et al. have already reported similar thermodynamic behavior of liquid crystal dimers and trimers [8–10].

CONCLUSION

A series of vinyl-substituted liquid crystal dimers **(1)** were prepared. The compounds **(1)** ($n = 3$–6) exhibited only nematic liquid crystalline behavior, while **1** ($n = 7$, 8, 10, and 12) showed both the nematic and smectic phases and **1** (n = 9 and 11) showed only the smectic phase. The entropy change associated with the smectic-nematic transition of **1** (n = 7) was very small, compared with those of **1** (n = 8, 10, and 12). The liquid crystalline properties of **1** were compared with those of BCBOn and the trimers **(2)**. Since BCBOn and **2** show the nematic phase but no smectic phase, the formation of the smectic phase of **1** may result from the existence of the vinyl group. The entropy changes associated with the nematic-isotropic and smectic-isotropic transitions of **1** definitely exhibited an odd–even effect as the number (k) of atoms in the flexible spacers was varied, in which the even numbers exhibited higher values. The odd–even effects of **1** resembled those of BCBOn and **2**, but the entropy changes associated with the nematic-isotropic transition of **1** exhibited lower values in comparison with those of BCBOn and **2**. The values of **1** were about half those of **2**. These results are consistent with the odd–even effects seen in the transitional behavior of the known liquid crystal dimers and trimers [1, 8–10].

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