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Effects of combining of different flexible spacers in liquid crystal trimers and tetramers on transition properties

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Liquid crystal trimers and tetramers containing two kinds of flexible spacers, namely $O(CH_2)_mO$ and $COO(CH_2)_nO$, were divided into four classes according to the odd/even nature of the number of atoms in the flexible spacers: specifically, even–even, odd–odd, even–odd, and odd–even trimers, and even–even–even, odd–odd–odd, odd–even–odd, and even–odd–even tetramers. The transition properties of the four types of trimers and of tetramers were compared. Although the nematic–isotropic transition temperature and the associated entropy changes were primarily related to the number of the even-membered flexible spacers in these molecules, the different combinations of the flexible spacers significantly affected their transition properties.

Keywords: liquid crystal trimers; liquid crystal tetramers; flexible spacers; transition properties

1. Introduction

Liquid crystal (LC) trimers and tetramers consist of molecules containing three and four mesogenic units joined by two and three flexible spacers, respectively [1–7]. These molecules exhibit a remarkable odd–even effect in their transition properties, which depends on the length and parity of the flexible spacer. The structure property relationships in LC trimers and tetramers have been studied by a number of researchers [1–20], and we have also studied odd–even effects in LC trimers **(1)** [21] and tetramers **(2)** [22]. The molecules **(1)** and **(2)** contain two kinds of flexible spacers, namely $O(CH_2)_mO$ and $COO(CH_2)_nO$ groups. Since trimers **(1)** are non-symmetric molecules, they were divided into four types, according to the odd/even nature of the number of atoms in the flexible spacers: specifically, even–even (e–e), odd–odd (o–o), even–odd (e–o), and odd–even (o–e). Schematic representations of these four types of trimer are depicted in Figure 1, in which the spacers are in all-*trans*-conformations. Similarly, LC tetramers **(2)** were divided into four types of tetramers: even–even–even (e–e–e), odd–odd–odd (o–o–o), even–odd–even (e–o–e), and odd–even–odd (o–e–o) (Figure 2).

LC dimers and oligomers are also of interest as model compounds for main chain LC polymers [1, 23, 24]. The effects of combining different flexible spacers in LC oligomers and polymers on their transition properties provides significant information regarding the structure property relationships [7]. Percec *et al.* [25] reported the transition properties of the LC copolymers containing odd- and even-membered flexible spacers. Henderson and Imrie reported the transition properties of the LC trimers [12] and the LC tetramers [13, 14] containing odd- and even-membered flexible spacers. In the present report, the transition properties of the four types of trimers and of tetramers were compared in order to elucidate an effect of combining of different flexible spacers in LC trimers **(1)** and tetramers **(2)**.

2. Experimental details

2.1 Characterisation

Elemental analyses were performed in the Analytical Center of Kyoto University. The ^1H 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. The IR spectra were recorded with a JASCO FT/IR-420 spectrometer. The 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. Microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Linkam LK-600PH).

2.2 Synthesis

The e–o and o–e trimers (Figure 1) were prepared according to the procedure described previously for the e–e and o–o trimers [21]. Similarly the e–o–e and o–e–o tetramers (Figure 2) were prepared according to

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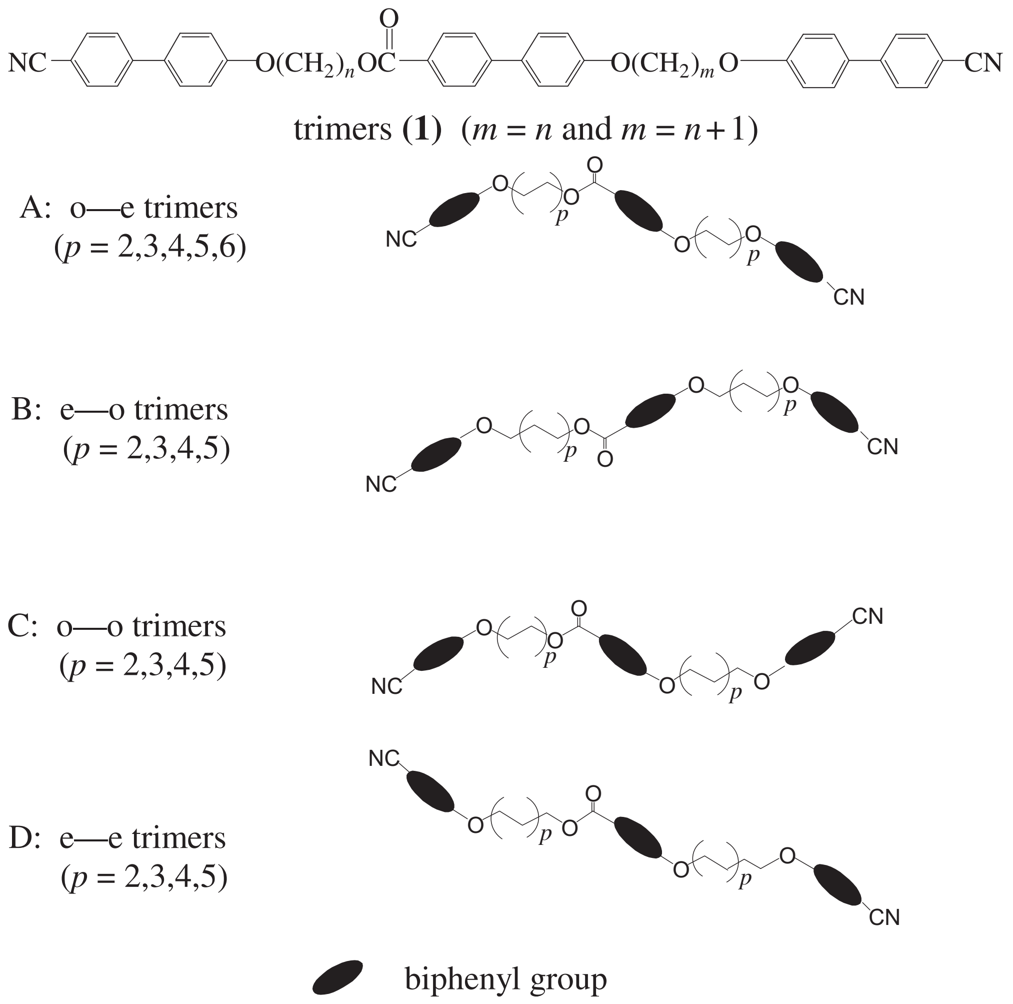

Figure 1. Structure of trimers **(1)** and schematic representations of four trimer types.

the procedure described elsewhere for the e–e–e and o–o–o tetramers [22]. All the structures of trimers **(1)** and tetramers **(2)** were characterised by elemental analyses, and IR and ^{1}H NMR spectral data.

Trimer **(1)** ($n = m = 4$). ^{1}H NMR (CDCl$_3$) δ 8.05 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.03–6.98 (m, 6H), 4.44 (broad, 2H), 4.11 (broad, 6H), 2.02 (broad, 8H). IR (CDCl$_3$) 2952, 2875, 2227(CN), 1714(CO), 1606, 1495, 1396, 1279, 1248, 1180 cm^{-1}. Elemental analysis: calcd for $C_{47}H_{40}N_2O_5$, C 79.19, H 5.66, N 3.93%; found, C 79.26, H 5.75, N 3.88%.

Tetramer **(2)** ($n = m = 4$). ^{1}H NMR (CDCl$_3$) δ 8.05 (d, 4H, $J = 8$ Hz), 7.7–7.5 (m, 20H), 7.00 (d, 4H, $J = 8$ Hz), 6.98 (d, 4H, $J = 8$ Hz), 4.43 (broad, 4H), 4.12 (broad, 8H), 2.1–2.0 (broad, 12H). IR (CDCl$_3$) 2952, 2873, 2227(CN), 1712(CO), 1606, 1495, 1471, 1277, 1248, 1182 cm^{-1}. Elemental analysis: calcd for $C_{64}H_{56}N_2O_8$, C 78.35, H 5.75, N 2.86%; found, C 78.52, H 5.81, N 2.84%.

See supplementary material for data on trimer **(1)** ($n = m = 5$–12) and tetramer **(2)** ($n = m = 5$–12), available via the multimedia link on the online article webpage.

3. Results and discussion

The transition properties of the e–e and o–o trimers [21] and of the e–e–e and o–o–o tetramers [22] have already been reported. The thermal behaviour of the new compounds, namely the o–e and e–o trimers and the o–e–o and e–o–e tetramers, was analysed by means of DSC and polarising microscopy. The o–e and e–o trimers exhibited only nematic behaviour. The nematic phases showed characteristic Schlieren optical textures. The o–e–o and e–o–e tetramers exhibited nematic (Schlieren texture) and/or SmA (focal-conic texture) behaviour. The transition properties of the new compounds are summarised in Table 1.

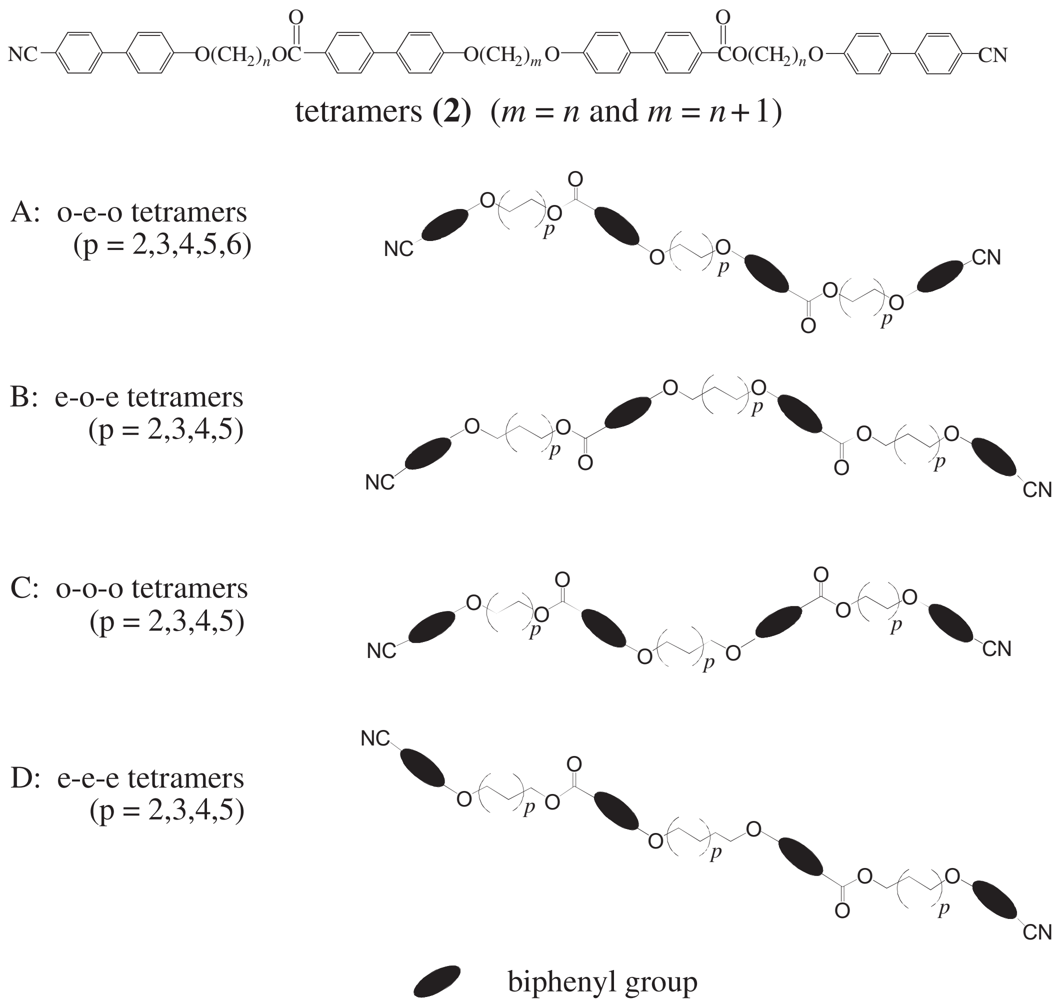

Figure 2. Structure of tetramers **(2)** and schematic representations of four tetramer types.

Trimers **(1)** contain $O(CH_2)_mO$ and $COO(CH_2)_nO$ groups as the flexible spacers. Figure 3 shows the dependence of transition temperature on the number (*n*) of methylene units in the $COO(CH_2)_nO$ group for the four types of trimers. The number (*m*) of methylene units in the $O(CH_2)_mO$ group is equal to the number (*n*) in Figure 3(a) (o–e trimers) and Figure 3(b) (e–o trimers), but is equal to $(n + 1)$ in Figure 3(c) (o–o trimers) and Figure 3(d) (e–e trimers). The transition temperature strongly depends on the number (*n*) of methylene units in the flexible spacers for four types of trimers.

The comparisons of the melting points and the nematic–isotropic transition temperatures among the four trimer types are shown in Figure 4 and Figure 5, respectively. In particular, the nematic–isotropic transition temperature clearly depends on the number (*n*) of methylene units. The e–e trimers exhibited the highest melting point and nematic–isotropic transition temperature of the four trimers types. In starting the present research, we were particularly interested in investigating whether there is a difference in the transition properties of the e–o and o–e trimers in the case of non-symmetric trimers such as **1**. It can be seen from Figure 5 that the nematic–isotropic transition temperature of the e–o trimers is similar to but a little higher than that of the o–e trimers. Therefore, the nematic–isotropic transition temperature of the e–e trimers, the e–o trimers, the o–e trimers and the o–o trimers decreases in that order.

The dependence of the entropy changes associated with the nematic–isotropic transition on the number (*n*) of methylene units in the $COO(CH_2)_nO$ group (Figure 6) also reveals a clear distinction among the four trimer types. The e–e trimers exhibited the highest values of the entropy change of the four types of trimers. The e–o trimers exhibited somewhat higher values of the entropy change than the o–e trimers. The values of the entropy change of the e–e, e–o, o–e and o–o trimers decreased in that order. This order is the same as obtained for the comparison of thenematic–isotropic transition temperature of the

Table 1. Transition temperature and associated entropy changes of trimers **(1)** ($n = m$) and tetramers **(2)** ($n = m$).

	n	Type	T_M/°C	T_{SN}/°C	T_{SI}/°C	T_{NI}/°C	ΔS_M/R	ΔS_{SN}/R	ΔS_{SI}/R	ΔS_{NI}/R
1	4	o–e	188			228	10.2			0.94
1	5	e–o	191			224	10.2			1.55
1	6	o–e	176			208	10.1			1.18
1	7	e–o	194			201	10.9			1.64
1	8	o–e	160			190	14.8			1.51
1	9	e–o	154			184	14.7			1.85
1	10	o–e	162			177	15.8			1.87
1	11	e–o	138			169	18.2			2.18
1	12	o–e	151			165	18.7			2.22
2	4	o–e–o	228			(214)	17.0			(0.58)
2	5	e–o–e	217			245	15.1			3.02
2	6	o–e–o	179			200	14.2			0.95
2	7	e–o–e	208	(194)		216	15.3	(0.72)		3.30
2	8	o–e–o	156	166		185	13.5	0.63		1.81
2	9	e–o–e	166	181		190	14.7	0.38		3.58
2	10	o–e–o	165		173		18.9		4.66	
2	11	e–o–e	147		178		16.1		3.88	
2	12	o–e–o	160		169		20.4		5.16	

Notes: n: number of methylene units in $COO(CH_2)_nO$ as flexible spacer.
T_M: melting point. T_{SN}: SmA–nematic transition temperature. T_{SI}: SmA–isotropic transition temperature. T_{NI}: nematic–isotropic transition temperature. ( ) upon cooling.

four types of trimers. The difference between the o–e and e–o trimers is caused by the position of ether and ester groups. The molecular shapes of the e–o trimers are similar to those of the o–e trimers. Therefore, it is thought that the differences in the transition properties between the e–o trimers and the o–e trimers result from the polarisability of these molecules.

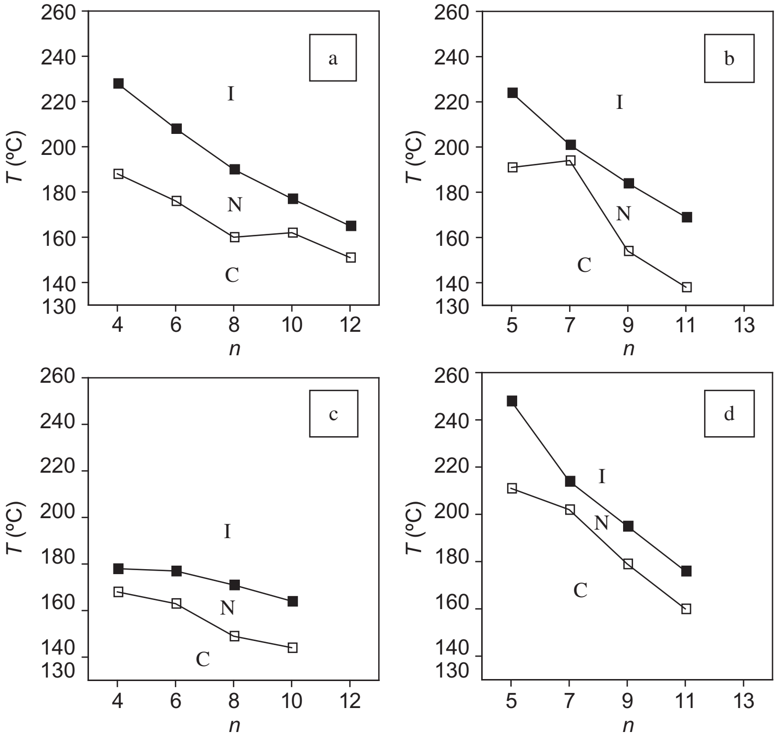

Figure 3. Dependence of transition temperature on the number (n) of methylene units in the $COO(CH_2)_nO$ group for four trimer types. (a) A: o–e trimers: **1** ($m = n$; $n = 4, 6, 8, 10, 12$). (b) B: e–o trimers: **1** ($m = n$; $n = 5, 7, 9, 11$). (c) C: o–o trimers: **1** ($m = n + 1$; $n = 4, 6, 8, 10$). (d) D: e–e trimers: **1** ($m = n + 1$; $n = 5, 7, 9, 11$). □: melting point. ■: nematic–isotropic.

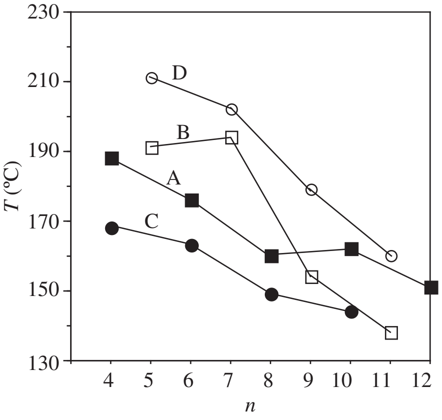

Figure 4. Dependence of melting point on the number (n) of methylene units in the COO(CH_2)$_n$O group for four trimer types. ■ A: o–e trimers. □ B: e–o trimers. ● C: o–o trimers. ○ D: e–e trimers.

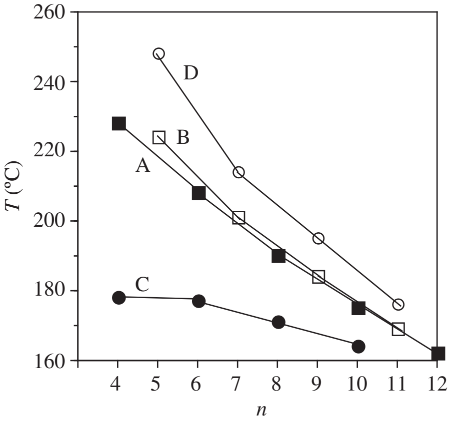

Figure 5. Dependence of nematic–isotropic transition temperature on the number (n) of methylene units in the COO(CH_2)$_n$O group for four trimer types. ■ A: o–e trimers. □ B: e–o trimers. ● C: o–o trimers. ○ D: e–e trimers.

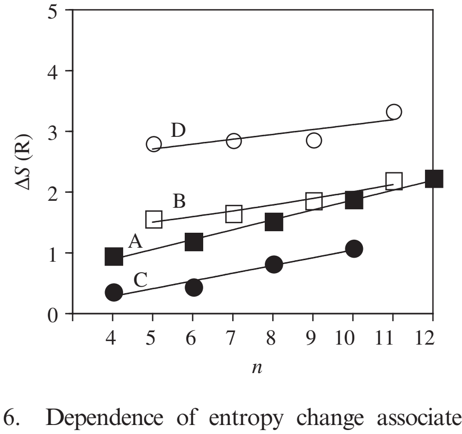

Figure 6. Dependence of entropy change associated with nematic–isotropic transition on the number (n) of methylene units in the COO(CH_2)$_n$O group for four trimer types. ■ A: o–e trimers. □ B: e–o trimers. ● C: o–o trimers. ○ D: e–e trimers.

Figure 7 shows the dependence of the phase transition temperature on the number (n) of methylene units for the four tetramer types. The number (m) is equal to the number (n) in Figure 7(a) (o–e–o tetramers) and Figure 7(b) (e–o–e tetramers), but is equal to ($n + 1$) in Figure 7(c) (o–o–o tetramers) and Figure 7(d) (e–e–e tetramers). Although tetramers **(2)** exhibited nematic and/or smectic phases, the nematic–isotropic transition temperature effectively depended on the number (n) of methylene units in the flexible spacers. Therefore, the nematic–isotropic transition temperature of the four tetramer types was compared (Figure 8), and the monotropic transition temperature was plotted for the o–o–o tetramer ($n = 4$) [22] and the o–e–o tetramer ($n = 4$) (Table 1). The nematic–isotropic transition temperature decreased in the order: e–e–e, e–o–e, o–e–o and o–o–o tetramers, although the temperature of the e–o–e tetramer ($n = 9$) was similar to that of the e–e–e tetramer ($n = 9$). These results suggest that the nematic–isotropic transition temperature of the LC tetramers is primarily related to the number of the even-membered (or odd-membered) flexible spacers in these molecules. This conclusion is consistent with the results of trimers **(1)**.

Although the dependence of the entropy changes associated with the melting point on the flexible spacers of the four tetramer types were similar (Table 1), Figure 9 reveals interesting differences in the entropy changes associated with the nematic–isotropic transition among the four types of tetramers. The entropy changes decreased in the order: e–e–e, e–o–e, o–e–o and o–o–o tetramers, and this order is the same as that obtained for the comparison of the nematic–isotropic transition temperature. However, it can be seen from Figure 9 that the dependence of the entropy changes may be divided into two groups: one group is the e–e–e and e–o–e tetramers, and the other is the o–e–o and o–o–o tetramers. The entropy changes of the e–o–e tetramers were similar to those of the e–e–e tetramers rather than those of the o–e–o tetramers. The e–e–e and e–o–e tetramers clearly exhibited higher values of the entropy change, compared with the o–o–o and o–e–o tetramers. Furthermore, the variations of the flexible spacers significantly affected the entropy changes of the o–o–o and o–e–o tetramers, compared with those of the e–e–e and e–o–e tetramers. The dependence of the entropy changes of the o–e–o tetramers on the flexible spacers was similar to that of the o–o–o tetramers. These results are consistent with the previous reports of LC copolymers [25] and LC tetramers [13, 14] containing odd- and even-membered flexible spacers. The remarkable difference between the e–o–e tetramers and the o–e–o tetramers is particularly interesting, because the difference is not completely understood on the basis of the number of the even-membered (or

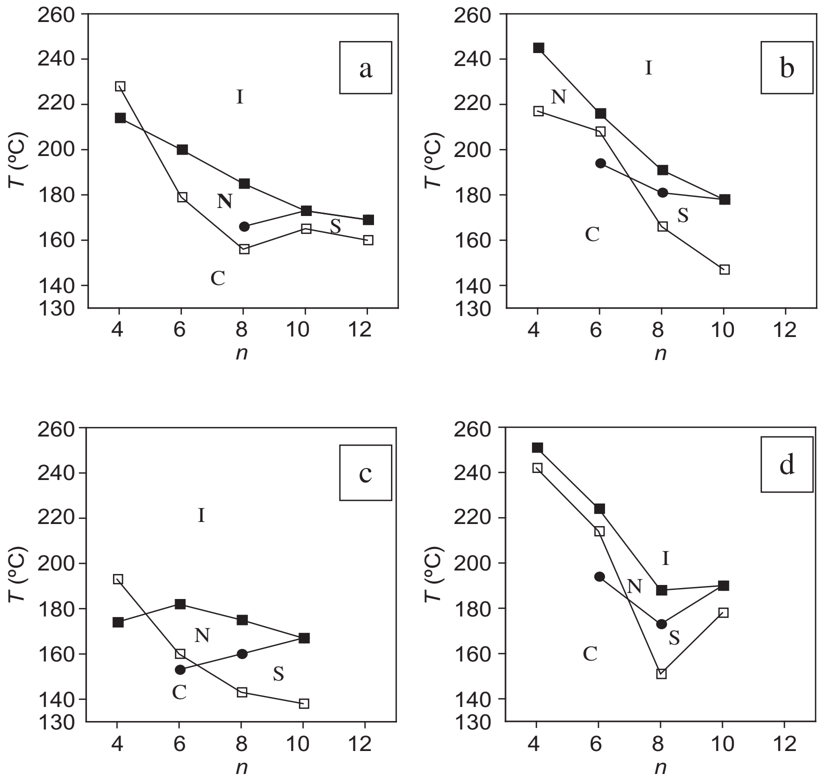

Figure 7. Dependence of transition temperature on the number (n) of methylene units in the COO(CH$_2$)$_n$O group for four tetramer types. (a) A: o–e–o tetramers: **2** ($m = n$; $n = 4, 6, 8, 10, 12$). (b) B: e–o–e tetramers: **2** ($m = n$; $n = 5, 7, 9, 11$). (c) C: o–o–o tetramers: **2** ($m = n + 1$; $n = 4, 6, 8, 10$). (d) D: e–e–e tetramers: **2** ($m = n + 1$; $n = 5, 7, 9, 11$). □: melting point. ■: nematic–isotropic or SmA–isotropic transition. ●: SmA–nematic transition.

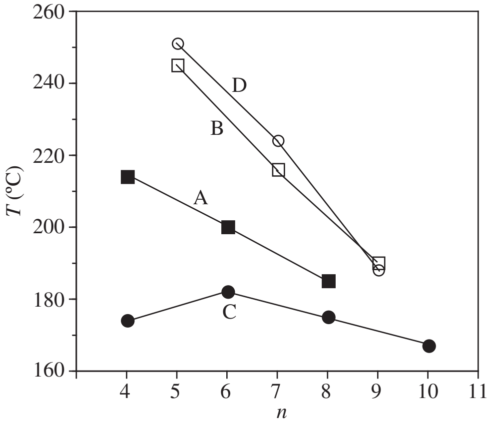

Figure 8. Dependence of nematic–isotropic transition temperature on the number (n) of methylene units in the COO(CH$_2$)$_n$O group for four tetramer types. The monotropic transition temperature was plotted for the o–o–o tetramer ($n = 4$) and the o–e–o tetramer ($n = 4$). ■ A: o–e–o tetramers. □ B: e–o–e tetramers. ● C: o–o–o tetramers. ○ D: e–e–e tetramers.

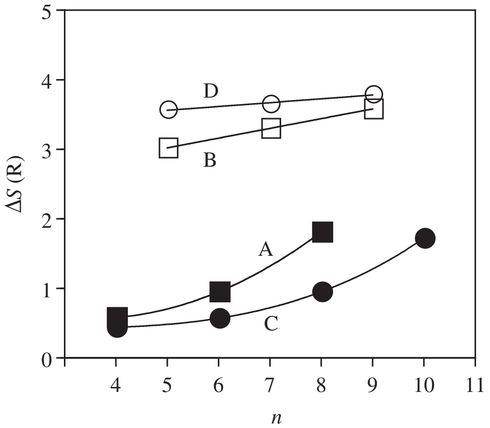

Figure 9. Dependence of entropy change associated with nematic–isotropic transition on the number (n) of methylene units in the COO(CH$_2$)$_n$O group for four tetramer types. ■ A: o–e–o tetramers. □ B: e–o–e tetramers. ● C: o–o–o tetramers. ○ D: e–e–e tetramers.

odd-membered) flexible spacers in these molecules. It is thought that the molecular shapes [7] and polarisabilities of LC tetramers are significantly related to the structural differences.

4. Conclusion

The transition properties of the e–e, o–o, e–o and o–e trimers, and the e–e–e, o–o–o, o–e–o and e–o–e tetramers were compared. The nematic–isotropic transition temperature and the associated entropy changes were primarily related to the number of the even-membered (or odd-membered) flexible spacers in these molecules. However, the e–o trimers exhibited somewhat higher values of both the nematic isotropic transition temperature and the associated entropy changes than those of the o–e trimers. For the tetramers, the e–e–e and e–o–e tetramers clearly exhibited higher values of the transition properties, compared with the o–o–o and o–e–o tetramers. Such differences are not completely understood on the basis of the number of the even-membered flexible spacers in these molecules. Therefore, it was concluded that the transition properties of trimers **(1)** and tetramers **(2)** are significantly dependent on the combinations of the different flexible spacers in these molecules.

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