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Novel Ferroelectric Liquid Crystals Derived from *n*-Alkyl Esters of (*R*)-3-Hydroxybutanoic Acid (II), the Correlation between Their Ferroelectric Properties and Their Molecular Structure

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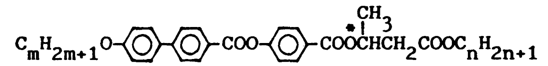
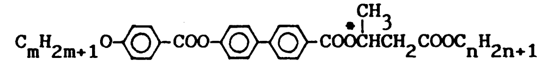
The temperature dependence of the spontaneous polarization (*Ps*) and the optical tilt angle (θ) of the following series of novel ferroelectric liquid crystals, derived from normal alkyl esters of (*R*)-3-hydroxybutanoic acid, have been investigated.


I(m,n)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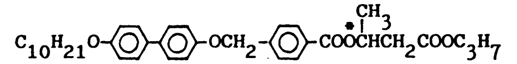
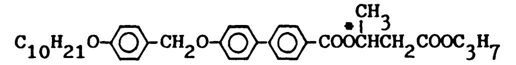

III(10,3)


IV(10,3)

The magnitude of *Ps* and θ depends on the kind of linkage groups and their position in the core moiety as well as on the lengths of both terminal chains. The *Ps*'s for **I**(*m*,*n*) and **II**(*m*,*n*) show a maximum at (*m*,*n*)=(10, 3), whereas their θ's increase with the *m* and do not change very much with *n*. In comparison with four analogues (**I(10,3)**, **II(10,3)**, **III(10,3)**, and **IV(10,3)**), which have the same terminal chains, but which show a different phase sequence, the magnitudes of *Ps* and θ are in the orders of: **III(10,3)**>**IV(10,3)**>**I(10,3)**~**II(10,3)** and **III(10,3)**> **I(10,3)**>**II(10,3)**>**IV(10,3)** respectively. Among all the compounds, the **III(10,3)** shows the maximum *Ps* as high as 1100 μC m^{-2} in the chiral smectic C phase and as high as 1750 μC m^{-2} in the chiral smectic I phase.

Ferroelectric liquid crystals are of great interest because of their application in a new type of high-speed switching device.[1] In the practical use of the liquid crystals, several smectogens have been blended in order to obtain a composition with properties suitable for the divice. For this purpose, it is necessary to know the material constants, such as the transition temperatures, the porality, the magnitude of spontaneous polarization (*Ps*), the optical tilt angle (θ), and the refractive index, and to understand the correlation between these physical properties and the molecular structure. Especially, it is important, not only from the practical point of view but also from the fundamental point of view, to elucidate the relationship between the two material constants (*Ps*,θ) and the molecular structure.

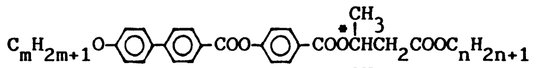
Ph. Martinot-Lagarde et al. showed simple formulae for the temperature dependence of *Ps* and θ for the compounds with a smectic A(SmA)-chiral smectic C(Sm*C) transition:[2]

$$Ps(T)=Ps^{\circ}(T_c-T)^a \qquad (1)$$

$$\theta(T)=\theta^{\circ}(T_c-T)^b \qquad (2)$$

where *Ps(T)* is the spontaneous polarization at temperature *T* °C, T_c is the SmA-Sm*C transition temperature, *T* is the actual temperature, $\theta(T)$ is the tilt angle at temperature *T* °C, and Ps°, θ°, *a*, and *b* are constants. These equations have been used in many papers; however, recent studies have shown that some materials do not exhibit the usual tendency in the temperature dependency of θ and *Ps* and that, therefore, the equations cannot be accepted as embodying general principles.[3–6] Furthermore, it has been recognized that the temperature dependency of θ in the SmC phase depends on the kind of phases adjacent to the Sm C phase.[7,8] In order to obtain a better understanding of the correlation between these material constants and the molecular structure, it is necessary to measure the material constants for various compounds and to accumulate data relating to the structural factors concerned with the ferroelectric properties.

We have synthesized the following series of novel ferroelectric liquid crytals, derived from *n*-alkyl esters of (*R*)-3-hydroxybutanoic acid, and investigated their physical properties: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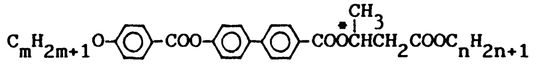
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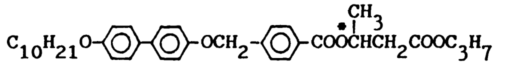
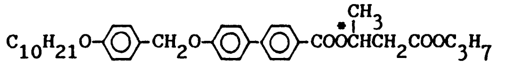

III(10,3)


IV(10,3)

One of these compounds **I(8,2)** has already been synthesized, and the temperature dependence of its *Ps* has been reported by Taniguchi et al.[9] However, no systematic investigation of the ferroelectric properties of the homologous series has yet been done.

In a previous paper,10) we reported a synthetic method and the mesomorphic properties of these homologous series. In this paper, we wish to report the temperature dependency of θ and Ps for these compounds and discuss the correlation between their ferroelectric properties and the molecular structures.

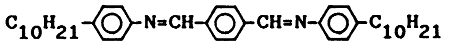
Experimental

Measurement of Physical Properties. Miscibility tests for the unidentified smectic phase below the Sm*C phase were carried out by mixing the compounds with standard materials whose phase sequences has been assigned and by observing the microscopic textures by means of a Nikon polarizing microscope equipped with a Mettler FP52 heating stage. The spontaneous polarization (*Ps*) was determined by a triangular-wave method reported by Miyasato et al.11) The frequency, the maximum amplitude, and the cell thickness were 10 Hz, ±150 V, and 50 μm, respectively. The optical tilt angle (θ°) and the polarity(the direction of *Ps*) were determined by applying a d.c. field to a specimen placed between crossed polarizers and by observing the direction of extinction by rotating the stage. The helical twist sense was determined by observing the variation in pitch in the Sm*C phase upon mixing with the reference compound.

Results and Discussion

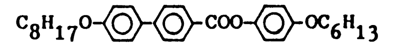
The mesomorphic transition temperatures and the phase sequences of the compounds used in the experiments are summarized in Table 1. In order to assign the unidentified smectic phases below the Sm*C, we carried out miscibility tests for the analogues, **I**(**10**,**3**), **II**(**10**,**3**), and **III**(**10**,**3**), by mixing them with the following standard materials:

Terephthalidene-bis-4-n-decylaniline (TBDA)



Iso→SmA→SmC→SmI→SmF→SmG

4-n-Hexyloxyphenyl 4'-n-octyloxybiphenyl-4-carboxylate (HPOBC)



Iso→Ne→SmA→SmC→SmB

The miscibility diagrams of the binary mixtures, **I**(**10**,**3**)-TBDA, **II**(**10**,**3**)-HPOBC, and **III**(**10**,**3**)-TBDA, are shown in Figs. 1, 2, and 3 respectively. As can be seen in the figures, the Sm3 phases of **II**(**10**,**3**) and **III**(**10**,**3**) are smectic B(SmB) and chiral smectic I(Sm*I), respectively. The Sm3 phase of **I**(**10**,**3**), which was speculated in the previous paper to be the Sm*I phase from the microscopic texture, is really chiral smectic G(Sm*G) or chiral smectic J(Sm*J). These two phases cannot be distinguished by only miscibility tests.

All the compounds used in the experiments show a

Table 1. Phase Sequences and Transition Temperatures for the **I**(***m***,***n***) and **II**(***m***,***n***) Homologous Series, and the **III**(**10**,**3**) and **IV**(10,3) Analogues

Homologous Series	Carbon No. (*m*,*n*)	Phase-transition temperature (°C)a)									
		Mp	Sm4		Sm3		Sm*C		SmA		Iso
	(7,3)	91.8				(74.9)B)	*	105.0	*	154.3	*
	(8,3)	96.8				(66.6)	*	112.0	*	147.0	*
	(9,3)	84.5				(57.1)	*	110.0	*	146.1	*
	(10,3)	78.6				(52.5)	*	110.5	*	137.9	*
	(11,3)	81.2						115.9	*	140.6	*
	(12,3)	81.3						114.1	*	136.1	*
I(***m***,***n***)	(14,3)	86.3						110.5	*	130.1	*
	(16,3)	87.2						108.2	*	126.9	*
	(10,1)	78.5		(64.0)	*	102.8	*	120.0	*	155.7	*
	(10,2)	88.1				(58.0)	*	120.0	*	146.1	*
	(10,4)	68.0				(50.2)	*	111.1	*	136.5	*
	(10,5)	70.9				(49.2)	*	95.9	*	129.6	*
	(10,8)	74.5						83.5	*	123.7	*
	(9,3)	92.2						(80.0)	*	129.2	*
	(10,3)	85.8				(56.6)	*	(84.0)	*	126.5	*
	(12,3)	77.2						93.0	*	122.8	*
II(***m***,***n***)	(14,3)	72.1				(49.3)	*	96.1	*	118.7	*
	(16,3)	72.2						96.5	*	116.0	*
	(10,2)	75.8				(46.3)	*	(62.5)	*	110.5	*
	(10,7)	76.3				(46.3)	*	(62.5)	*	110.5	*
III(***m***,***n***)	(10,3)	85.4		85.4	*	110.5c)	*			127.0	*
IV(***m***,***n***)	(10,3)	90.0						(84.0)	*	93.6	*

a) Mp; melting point, Sm3, Sm4; unidentified smectic phase, Sm*C chiral smectic C, SmA; smectic A, Iso; isotropic liquid. b) ( ); monotropic transition. c) This transition was designated as Sm2-Sm*C in a previous paper.10)

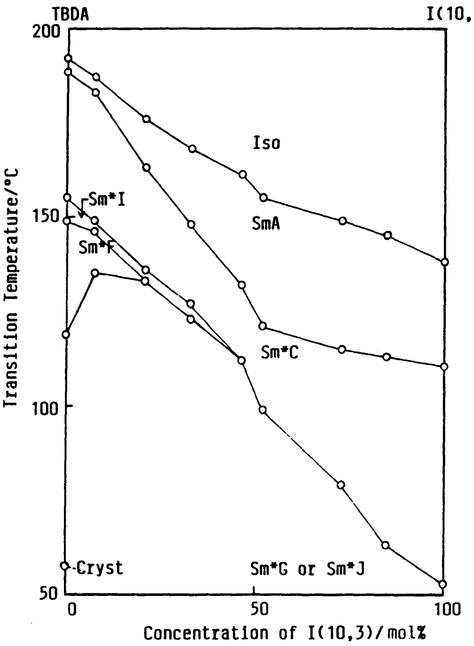


Fig. 1. Phase diagram for the binary mixtures of **I(10,3)** with TBDA.

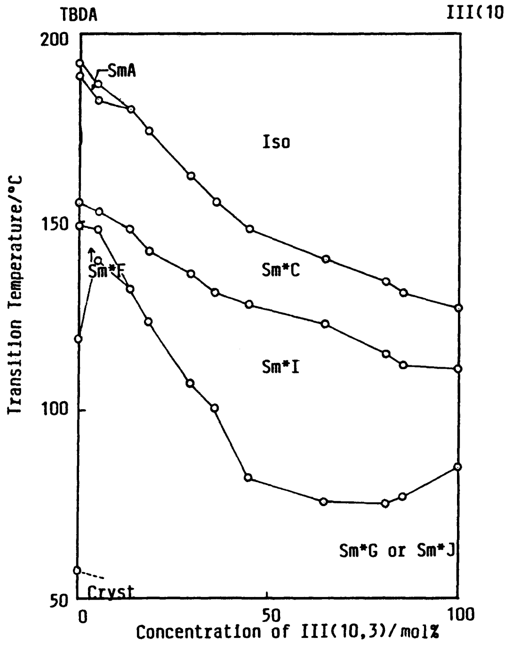


Fig. 3. Phase diagram for the binary mixtures of **III(10,3)** with TBDA.

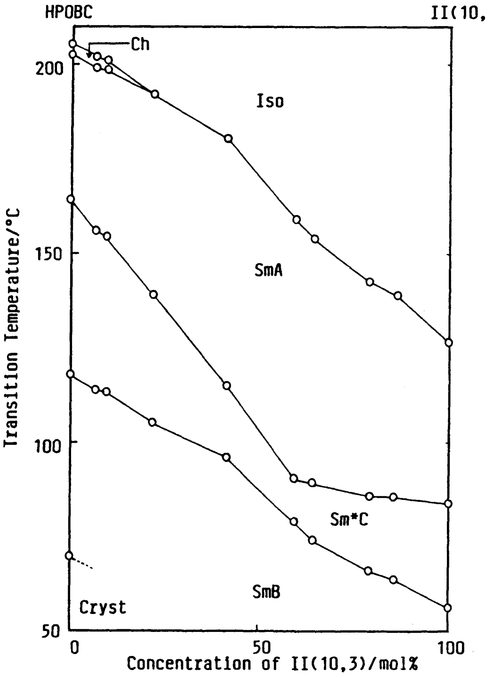


Fig. 2. Phase diagram for the binary mixtures of **II(10,3)** with HPOBC.

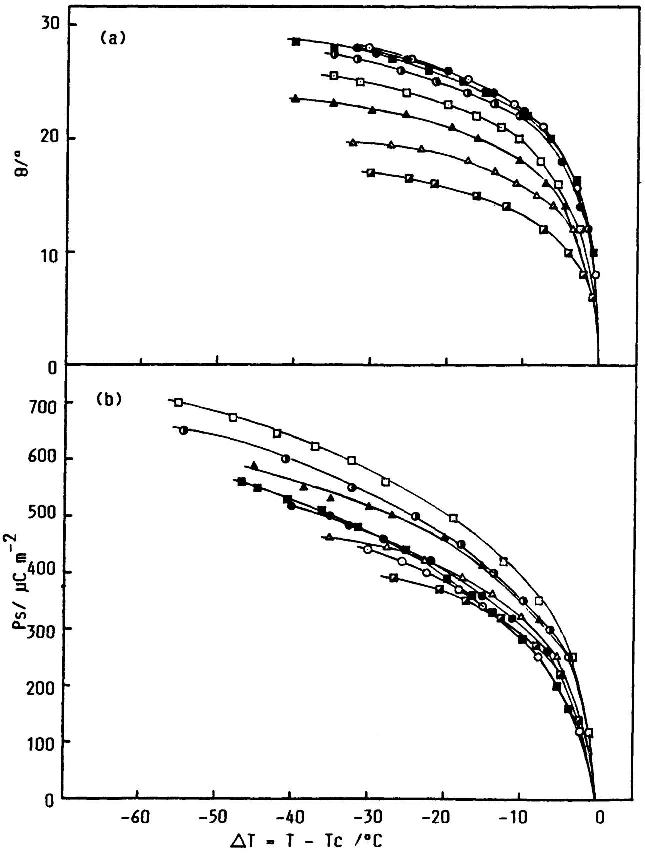


Fig. 4. Temperature dependence of the optical tilt angle (θ°) (a) and the spontaneous polarization (*Ps*) (b) for the homologous series **I(*m*,3)**: *m*=7 (—◪—); *m*=8 (—△—); *m*=9 (—▲—); *m*=10 (—□—); *m*=11 (—◑—); *m*=12 (—□—); *m*=14 (—●—); *m*=16 (—○—).

negative polarity and have a left-hand helix in the Sm*C phase. This tendency is consistent with the empirical rule about the relation between the absolute spatial configuration of a chiral group and the polarity and helical twist sense reported by Goodby et al.[12,13]

Figures 4(a,b) and 5(a,b) show the tempereature dependence of θ and *Ps* for the **I(*m*,3)** and **I(10,*n*)**

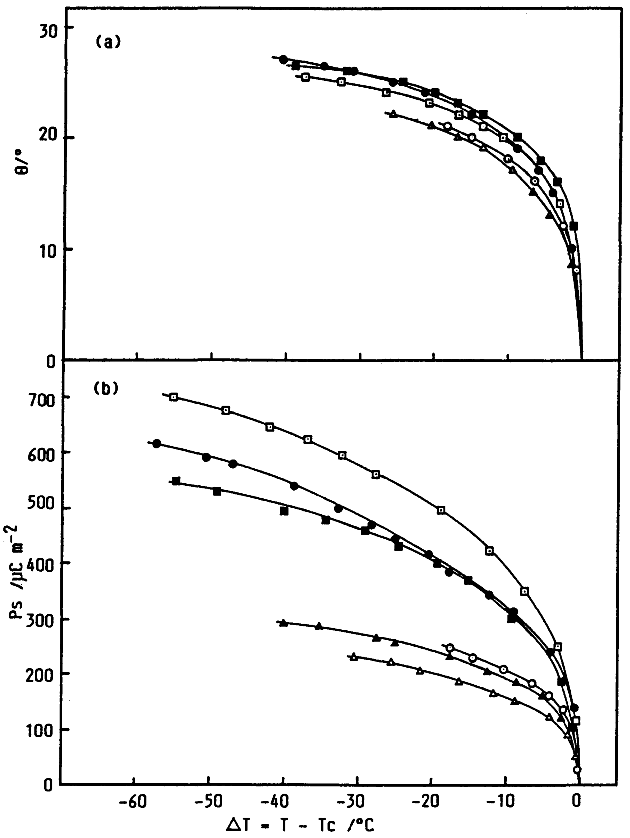


Fig. 5. Temperature dependence of the optical tilt angle (θ°) (a) and the spontaneous polarization (*Ps*) (b) for the homologous series **I(10,*n*)** *n*=1 (—○—); *n*=2 (—●—); *n*=3 (—□—); *n*=4 (—■—); *n*=5 (—▲—); *n*=8 (—△—).

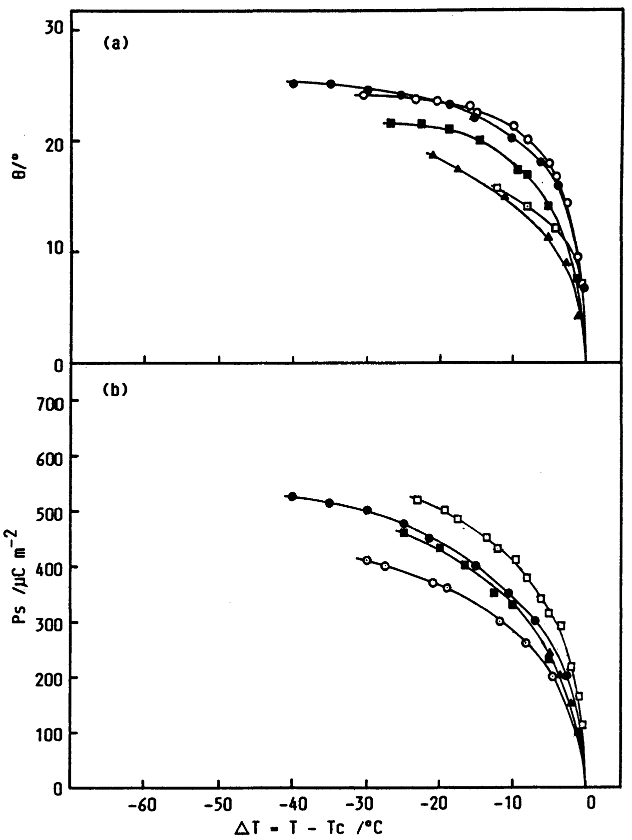


Fig. 6. Temperature dependence of the optical tilt angle (θ°) (a) and the spontaneous polarization (*Ps*) (b) for the homologous series **II(*m*,3)**: *m*=9 (—▲—); *m*=10 (—□—); *m*=12 (—■—); *m*=14 (—●—); *m*=16 (—○—).

homologous series, respectively. As is evident from the figures, the θ for **I(*m*,3)** increases with the number of carbon atoms (*m*) in the terminal alkoxyl chain and approaches a constant value (ca. 28°), whereas the *Ps* for **I(*m*,3)** increases with *m* up to *m*=10 and then decreases with *m*. The maximum *Ps* value (700 μC m^{-2}) was observed in the **I(10,3)** at $\Delta T=-55$°C. On the other hand, the θ for **I(10,*n*)** slightly increases with *n* up to *n*=4 and then gradually decreases with *n*, whereas the *Ps* for **I(10,*n*)** abruptly increase with *n* up to *n*=3 and then rapidly decrease with *n*. Figures 6(a,b) and 7(a,b) show the temperature dependence of the θ and *Ps* values for the **II(*m*,3)** and **II(10,*n*)** homologous series, respectively. These series have the same linkage group (-COO-) as the **I(*m*,3)** and **I(10,*n*)** except for its position in the core moiety. We could not measure the θ and *Ps* values for all the homologues because the majority of their Sm*C phases were unstable monotropic phases and because recrystallization often occurred during the measurements. The θ for **II(*m*,3)** also increases with *m* and approaches a constant value (ca. 25 °C), whereas the *Ps* for **II(*m*,3)** increases with *m* up to *m*=3 and then decreases with *m*. The maximum *Ps* (520 μC m^{-2} was observed in the **II(14,3)** at $\Delta T=-40$ °C. In the case of **II(10,*n*)** (Fig. 7(a,b)), the effect of the chain length (*n*) on the temperature dependency of θ and *Ps* cannot be clarified because the θ and *Ps* have been measured in only a few of the **II(10,*n*)**.

In order to elucidate the effect of the length of the terminal chains (*m,n*) on the θ and *Ps* for **I(*m*,*n*)** and **II(*m*,*n*)**, the values of θ and *Ps* at $\Delta T=-10$ °C were plotted against the carbon number (*m* and *n*) in the terminal chains (Figs. 8A(a,b) and 8B(a,b)). As can be seen in the figures, in the case of **I(*m*,*n*)**, the dependencies of the lengths of the two terminal chains (*m,n*) on the θ and *Ps* are significantly different from one another. The θ for **I(*m*,3)** increases with *m*, whereas that for **I(10,*n*)** does not change very much with *n*. On the other hand, the *Ps* values for **I(*m*,3)** and **I(10,*n*)** show maxima at *m*=10 and *n*=3, respectively. Moreover, the effect of *n* on the magnitude of *Ps* is stronger than that of *m* on the magnitude of *Ps*. A similar tendency can be seen in the **II(*m*,*n*)** except for the dependency of *n* on the θ for **II(10,*n*)** whose θ is much smaller than that of **I(10,*n*)**; that is, the effect of *m* on the θ and *Ps* for **II(*m*,3)** is almost the same as that for **I(*m*,3)**. The effect of *n* on the *Ps* for **I(10,*n*)**, although there are only two data plotted on the figure.

These results indicate that the structural factors

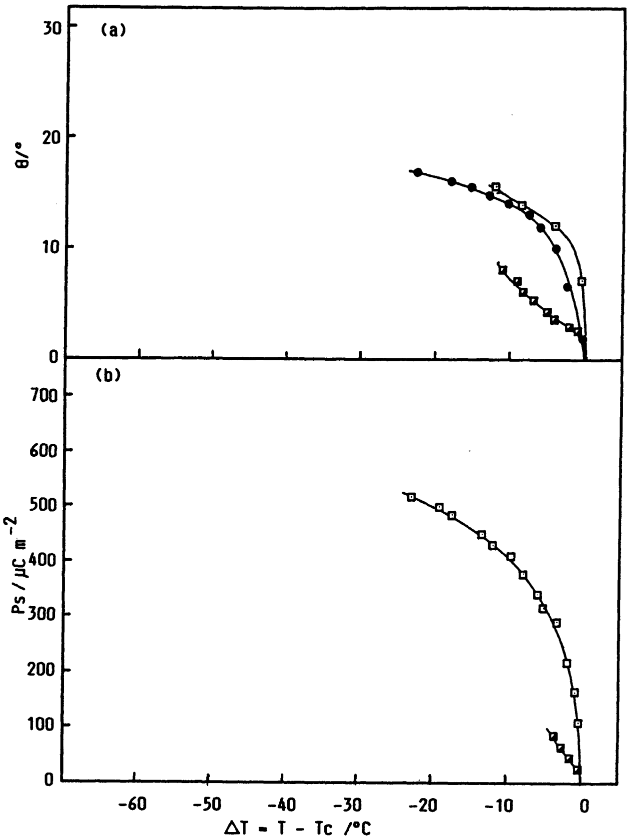


Fig. 7. Temperature dependence of the optical tilt angle (θ°) (a) and the spontaneous polarization (*Ps*) (b) for the homologous series **II(10,*n*)**: n=2 (—●—); n=3 (—□—); n=7 (—◪—).

concerned with the temperature dependency of the terminal chains on the *Ps* are quite different from those concerned with the temperature dependency of the terminal chains on the θ and that the constants, a and b, in Eqs. 1 and 2 are generally not equal. Additionally, judging from these data, the magnitude of *Ps* seems to be independent of the position of the linkage group -COO- in the core.

For the purpose of investigating more closely the effect of the core structure on the *Ps* and θ, the temperature dependence of *Ps* and θ for four analogues, **I(10,3)**, **II(10,3)**, **III(10,3)**, and **IV(10,3)**, were examined (Fig. 9). It is noteworthy that these analogues have different phase sequences. As is evident from the figures, the magnitudes of *Ps* and θ depend strongly on the core structures, that is, the kind and position of the linkage group in the core, and are in the orders of **III(10,3)**>**IV(10,3)**>**I(10,3)**~**II(10,3)** and **III(10,3)**> **I(10,3)**>**II(10,3)**>**IV(10,3)**, respectively. Among all the compounds used in the experiments, the **III(10,3)** with a -OCH_2- linkage shows the largest values of *Ps* and θ. Especially, the magnitude of *Ps* is as high as 1100 μC m^{-2} in the Sm*C phase and 1750 μC m^{-2} in the Sm*I phase.

Generally, the magnitude of *Ps* is considered to depend on the perpendicular component of the dipole moment of the polar group adjacent to the chiral part. These four analogues have the same group adjacent to the same chiral group; therefore, the origin of the *Ps* is considered to be same. Even if we take into consideration the difference in other factors (θ and T_c) con-

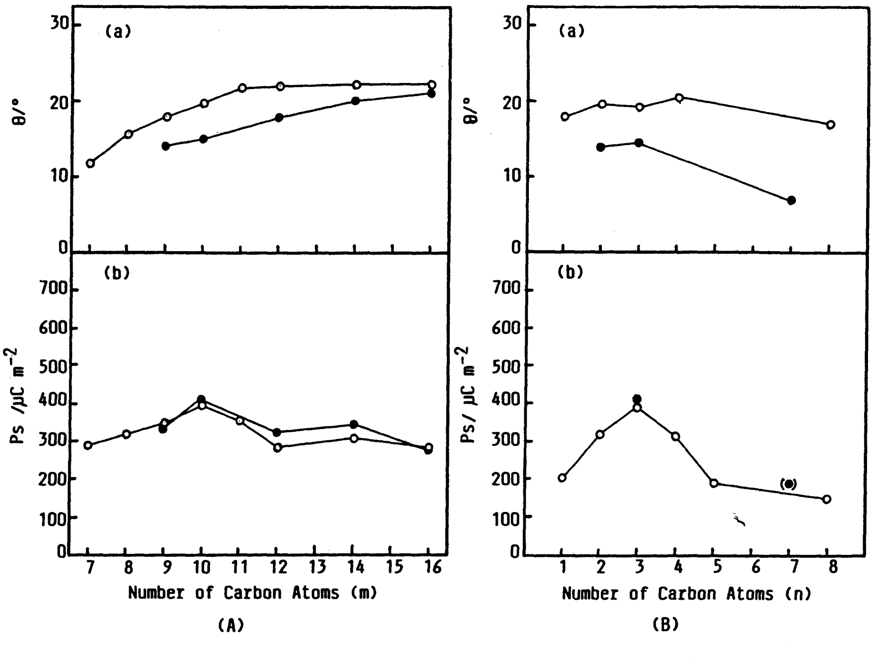


Fig. 8. Plots of the θ (a) and *Ps* (b) measured at ΔT=−10 °C against the number of carbon atoms (m) in the alkoxyl chain (n=3) (A) and the number of the carbon atoms (n) in the alkyl ester chain (m=10) (B): **I(*m*,*n*)** homologues (—○—); **II(*m*,*n*)** homologues (—●—). *( ): extrapolated value.

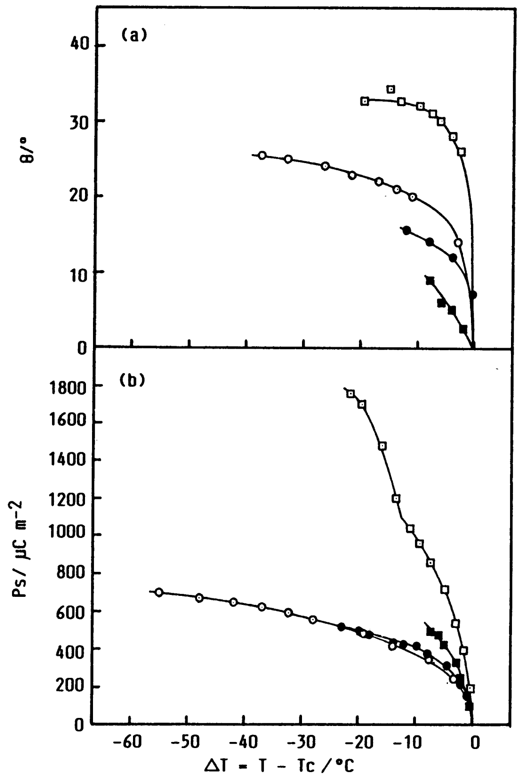
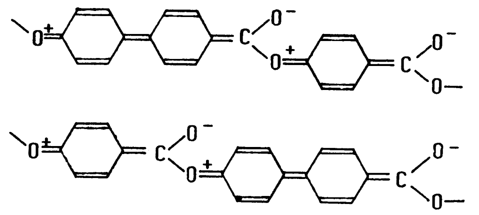


Fig. 9. Temperature dependence of the θ (a) and the *Ps* (b) for four analogues: **I(10,3)** (—○—); **II(10,3)** (—●—); **III(10,3)** (—□—); **IV(10,3)**.

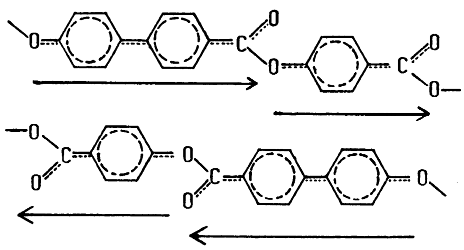
nected to the magnitude of *Ps*, we cannot explain the reason for the difference in the magnitude of *Ps* among these analogues.

Taniguchi et al. investigated the effect of linkage groups (-COO- and -CH_2O-) in the core on the *Ps* for four couples, each of which was a pair of analogues with the same chiral group, and showed that the compounds with the -COO- linkage had larger *Ps* values than those with the -CH_2O- linkage, except for one couple.[14] They speculated that the -COO- linkage enhanced the *Ps* more than the -CH_2O- linkage because of its larger dipole moment, although they did not measure the effect of θ on the *Ps*. Taking the effect of θ on the magnitude of *Ps* into consideration, among the four analogues investigated in this study, the **III(10,3)** and **IV(10,3)** with the -CH_2O- linkage show much larger *Ps* value than of the **I(10,3)** and **II(10,3)**; therefore, in this case, the -CH_2O- linkage seems to enhance the *Ps* more than the -COO- linkage. Similar results were also obtained in the mesogenic compounds with -CH_2O- linkage in the same core as that of **III(10,3)**.[15]

There is another difference in the natures of the -CH_2O- and -COO- bonds. Compared with the -CH_2O- bond, the -COO- bond is conjugated to the phenyl or biphenyl moiety in the core, leading to the production of induced dipole moments parallel to the molecular axis, as is shown in the following picture:



As has been pointed out by Goodby,[16] these induced dipoles cannot contribute to the *Ps*, but they do promote the following anti-parallel paking among the core moiety:



The formation of an anti-parallel pair could enhance the thermal stability of the Sm*C phase and also affect the temperature dependencies of *Ps* and θ in the Sm*C phase because of the intermolecular force attributed to the induced dipoles could suppress the interaction between the out-board dipoles and disturb the arrangement of the dipoles, thus contributing to the magnitude of *Ps*. Such difference in the intermolecular interactions may also affect the formation of higher-order smectic phases; that is, the packing state of the molecules in the Sm*C phase may some relation to the kinds of smectic phase below the Sm*C phase.

More detailed studies of the higher-order structures in smectic mesophase, including the effect of induced dipoles in the core, will be necessary to elucidate the correlation between the ferroelectric properties and the molecular structure.

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