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Synthesis and Thermal Properties of Novel Polymer Liquid Crystals having a Laterally-attached Liquid Crystalline Core at the Side Chain

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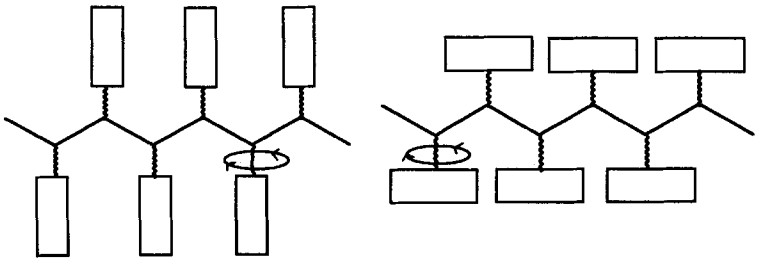
Synthesis and thermal properties of ω-[2-(4-*X*-phenoxycarbonyl)phenoxycarbonyl)-5-alkoxyphenoxy]alkyl and ω-[2-(4-*X*-phenoxycarbonyl)-5-alkoxyphenoxyalkyl poly-acrylates (*X* = *n*-alkoxyl or cyano group) have been reported. The homologs show a nematic phase, and a smectic phase as well as the nematic one is also formed when both terminal alkoxy chains of the core moiety are suitably long. On the cooling process, all the derivatives form a glassy phase corresponding to the prestates. The results will be discussed in terms of the molecular structure.

Keywords: Polymer liquid crystals, Synthesis, Thermal properties, Glassy transformation.

INTRODUCTION

Polymer liquid crystals have a hard and linear core simlar to usual liquid crystals and may be classified into three kinds—main chain, side chain, and their composite types-according to the difference in the location of the core moiety.[1] The side chain types may be roughly classified into two types, as shown below.



(A) (B)

For class A, the liquid crystal core is connected with the main chain by the spacer chain at the terminal position of the long molecular axis. A lot of polymer liquid

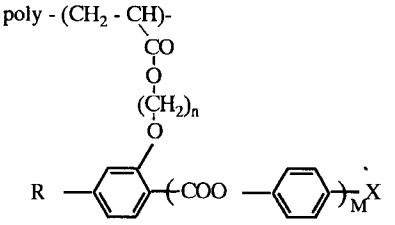
crystals belonging to this class have been synthesized.[2] Polymer liquid crystals of class B were first synthesized by Finkelmann *et al.*,[3] and a lot of related polymers have been extensively prepared.[4-11]

The usual liquid crystals in display devices keep rotational freedom along both longitudinal and transverse axes of the molecule. The rotational freedoms make possible the light valve function in a liquid crystal cell. In the core of polymer liquid crystals belonging to class A, the rotation along the longitudinal axis would be fairly restricted, though that along the transverse one is free. It has been attempted to apply this kind of polymers in display and recording devices.[12]

In class *B*, on the other hand, the rotation along the longitudinal direction would be easy if surroundings around the core were not so dense, and the rotation around the transverse direction would be restricted, giving rise to a biaxial nature in the optical properties.[7]

We can expect that the polymer liquid crystals of class *B* are applicable for display devices similar to the TN type's liquid crystals.

In order to develop polymer liquid crystals sensible to the electric field, we tried to synthesize the following related compounds.



Compound 1 M = 1, R, X = alkoxy
Compound 2 M = 1, R = alkoxy, X = CN
Compound 3 M = 2, R, X = alkoxy
Compound 4 M = 2, R = alkoxy, X = CN

n = 4, 5, 8, 12

The liquid crystal core cosists of two or three aromatic rings, the two ester groups are both arranged in the same direction, and the terminal cyano group in some derivatives, in oder to increase the anisotropy of the dielectric properties.

EXPERIMENTAL

Syntheses of monomers were reported in a previous paper,[13] and the polymers were synthesized by ordinal radical polymerization. *Poly-δ-[2-{4-butoxyphenoxycarbonyl)-phenoxycarbonyl}-5-butoxy]phenoxybutyl acrylate* (3*a*); A degassed solution of δ-[2-{4-(4-butoxyphenoxycarbonyl)phenoxycarbonyl}-5-butoxy]phenoxybutyl acrylate (5.0 g, 8.3×10^{-3} mol) and freshly recrystallized 2,2′-azobis (isobutylonitrile) (6.8 mg, 4.13×10^{-5} mol) in benzene (32 ml) was heated at 70°C for 5 hrs. The reaction mixture

was poured onto methanol (300 ml) and the resulting solution stood overnight at a room temperature. The precipitates were collected by decantation, and dissolved in benzene (10 ml). The solution was poured onto methanol (300 ml) and the resulting solution stood for overnight. The precipitates were collected by decantation. Reprecipitation was repeated more two times. The final precipitates were dried under vaccuo. The molecular weight of the polymer was assumed to be 15000 based on the standard poly-styrene by using GPC; Gain: 2.3 g.

The other polymers were prepared by a similar method, and the molecular weights were in the range between 13000 and 17000. Method: Phase transitions were observed by using a Nikon Model POH polarizing microscope fitted with a Mettler EP52 heating stage. Transition temperatures and the latent heats were measured with a Seiko–Denshi SSC-5200 differential scanning calorimeter (DSC), where indium (99.9%) was used as a calibration standard with the corresponding heating and cooling rates (mp. 156.6°C, $\Delta H = 6.80$ mcal/mg at a heating rate of 5°C/min).

RESULTS AND DISCUSSION

The typical DSC thermograms are shown in Figure 1. Figure 1 shows the DSC thermograms for *3f* and the corresponding monomer. The monomer shows an exotherm at 50°C (1.7 kJ/mol) due to *I–N* transition and at ca. 15°C due to the recrystallization in the cooling process (Figure 1a). The monomer shows only an endotherm around 60°C due to the melting phenomenon in the heating process (Figure 1b). On the other hand, *3f* shows an exotherm at 59°C due to the *I–N* transition and 30°C due to the *N–S* transition in the cooling process (Figure 1c). In addition, the DSC thermogram shows a remarkable deviation of the base line in the range between 10 and −10°C due to a glassy transformation of the *S* phase. An enantiotropic change is observed in the heating process, as shown in Figure 1d. As mentioned in a previous paper,[14] the bulky group at the lateral position is concerned with the glassy transformation. Interestingly, the remarkable change of the base line is also observed in the solidifying and melting processes, as shown in Figures 1a and 1b. In addition, the gap of the base line for the recrystallization in Figure 1a is close to that for the glassy transformation in Figure 1c. A similar phenomenon is observed in the heating processes in Figures 1b and 1d. These facts indicate that a similar change in the molecular shape occurs in both the glassy transformation and the recrystallization processes corresponding to the prestates.

The thermal properties are summarized in Tables 1–3.

Compounds *1* and *2* have two aromatic rings within the liquid crystalline core. The homologs having long alkoxyl groups at both terminal positions, *1*, show a nematic phase (*N*). The *N* phase shows a schlieren texture.

All the derivatives show difficulty in forming the crystalline phase, and show the glassy phase corresponding to the prestates in the cooling process. The cyano derivatives also show the glassy phase without showing any mesomorphic phase. Interestingly, the temperatures of the glassy transformation are lower than those of the corresponding alkoxy derivatives, *1*.

TABLE 1
Transition Temperatures and Latent Heats

Compound	R	X	n	T_g	N		I	ΔH(mJ/mg) N–I
1a	$C_5H_{11}O$	$C_5H_{11}O$	6	− 6	—		—	
1b[*1]	$C_8H_{17}O$	$C_8H_{17}O$	12	− 14	·	10	·	8
1c	$C_{12}H_{25}O$	$C_{12}H_{25}O$	12	− 8	·	16	·	12
2a	$C_8H_{17}O$	CN	6	4	—		—	
2b	$C_{12}H_{25}O$	CN	6	8	—		—	
2c	$C_8H_{17}O$	CN	12	14	—		—	

*[1] The crystalline form could not be observed.

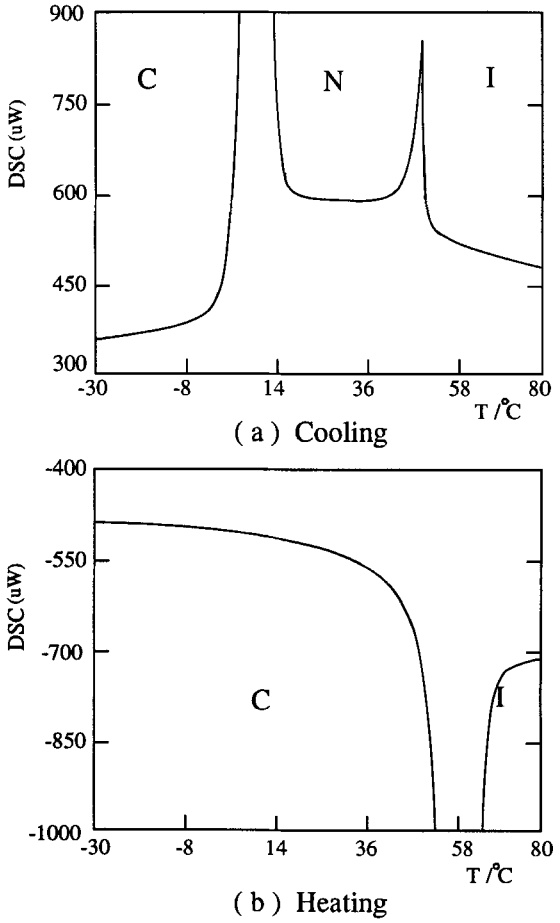
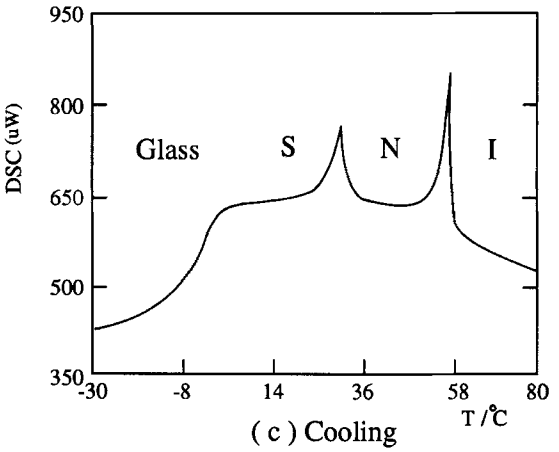
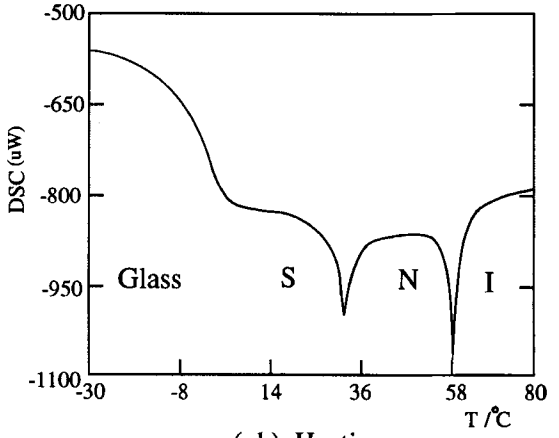


FIGURE 1 The DSC thermograms for compound *3f* on the cooling (a) and heating (b) processes, and for the monomer of *3f* on the cooling (c) and heating (d) ones. The DSC thermogram was operated at the cooling and heating rates of 5°C min.



(c) Cooling



(d) Heating

FIGURE 1 *(Continued)*

TABLE 2
Transition Temperatures and Latent Heats for Compound *3*

Compounds	*R*	*X*	*n*	T_g	*C*	*S*	*N*	*I*	ΔH (mJ/mg) *C–N*	*S–N*	*N–I*
3a	C_4H_9O	C_4H_9O	4	23	–	–	·	70 ·			1.5
3b	C_4H_9O	C_4H_9O	6	23	–	–	·	61 ·			1.0
3c	C_4H_9O	C_4H_9O	12	−9	–	–	·	41 ·			0.4
3d	$C_8H_{17}O$	$C_8H_{17}O$	4	18	–	–	·	70 ·			0.4
3e	$C_8H_{17}O$	$C_8H_{17}O$	6	2	–	–	·	45 ·			0.3
3f	$C_8H_{17}O$	$C_8H_{17}O$	12	−2	–	·	30 ·	59 ·		1.6	1.5
3g	$C_{12}H_{25}O$	$C_{12}H_{25}O$	4	33	–	–	·	116 ·			2.9
3h	$C_{12}H_{25}O$	$C_{12}H_{25}O$	6	6	–	–	·	76 ·			1.4
3i	$C_{12}H_{25}O$	$C_{12}H_{25}O$	12	6	·	42(·35)	·	55 ·	13.5	0.4	1.0

TABLE 3
Transition Temperatures and Latent Heats

Compound	R	X	n	T_g	C		N		I	ΔH(mJ/mg) C–N	ΔH(mJ/mg) N–I
4a	C_4H_9O	CN	4	31	–		· 93	·			0.2
4b	C_4H_9O	CN	6	34	–		· 57	·			0.2
4c	C_4H_9O	CN	12	23	–		· 51	·			0.5
4d	$C_8H_{17}O$	CN	4	33	–		· 75	·			0.4
4e	$C_8H_{17}O$	CN	6	24	–		· 54	·			0.6
4f	$C_8H_{17}O$	CN	12	13	–		· 50	·			1.5
4g	$C_{12}H_{25}O$	CN	4	35	–	39	· 87	·		7.5	0.1
4h	$C_{12}H_{25}O$	CN	6	30	–	35	· 70	·		6.4	0.7
4i	$C_{12}H_{25}O$	CN	12	14	·	34	· 48	·		25.2	1.7

Compounds *3* having three aromatic rings within the core show an *N* phase, and the homologs having long terminal- and spacer-alkoxyl groups show a smectic (*S*) phase as well as the *N* one. The textures of these phases are shown in Figure 2.

In Figure 2 the textures of those phases for *3i* and the corresponding monomer are shown for comparison. As we can see from the pictures, the textures of both monomer and polymer are quite similar to each other, where the *S* phase was assigned to the smectic $A(S_A)$ phase. Interestingly, the textures of both *S* phases are fairly broken and have fine brushes.

The liquid crystallinity is closely correlated with the molecular structure. For compound *1*, only an *N* phase is observed in the derivatives having long alkoxyl groups at both terminal positions. Probably, the geometrical anisotropy for the two-ring system linked by the ester linkage is insufficient for displaying the mesomorphic properties, and the long alkoxyl groups at the terminal positions might increase the anisotropy of the molecular geometry. Compound 2 is non-mesogenic, probably due to the lack of the geometrical anisotropy around the mesogenic core. All derivatives of compound *3* show the liquid crystalline phases, and the mesophase stabilities are dependent on the chain length of the alkyl chain in both terminal and spacer groups. The *N–I* transition temperature tends to decrease with elongating the spacer chain and increase with elongating the terminal alkoxyl chains. Derivatives *3f* and *3i* show an *S* phase as well as an *N* one. This fact indicates that the long spacer and both terminal chains play some important role in the formation of the layer arrangement.

A similar trend is observed in the cyano compound, *4*, where the *S* phase is not formed.

The miscibility of the mesophases was investigated by binary phase diagrams, as shown in Figure 3.

Figure 3a shows the binary phase diagram for *N*-(4-cyanobenzylidene)-4-octyloxyaniline (CBOOA) and *3f*. The mixture corresponds to the so-called "polar-non-polar" system of small molecules. Similar to usual mixtures,[15] the S_A–*N* transition shows an upward swelling in the region of an excess CBOOA. In point of microscopic

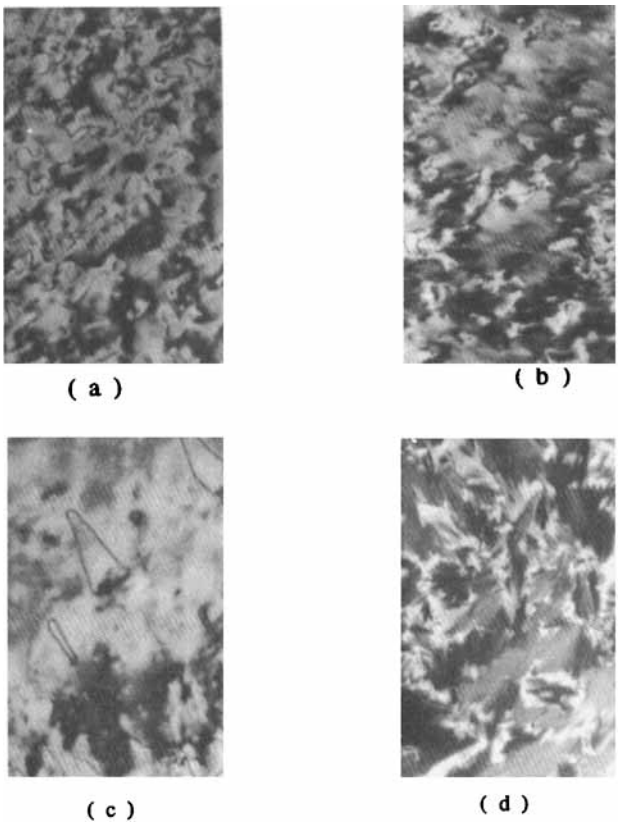


FIGURE 2 Micrographs of textures for the nematic (a) and smectic (b) phases of *3i*, and the nematic (c) and smectic *A*(*d*) ones of the monomer of *3i*. See Color Plate V.

observation, the mixture appears to be homogeneous in the isotropic liquid and liquid crystalline states. A similar phenomenon has been reported by Leube *et al.*[7] Figure 3b shows the binary phase diagram for the mixture of CBOOA and *4i*. The nematic phase has a heterogeneous region as well as the homogeneous one, probably due to a lack of affinity of both components. The S_A–N transition temperature for CBOOA rapidly reduces on increasing the concentration of *4i*, indicating that it is difficult for *4i* to form such a smectic layer as a partially bilayer arrangement. The solid phase shows an eutectic feature, though the line does not fit the le Chatelier–Schroder–van Laar equations.[16] Figure 3c shows the binary phase diagram for the mixture of *4f* and the monomer. While both components have the some liquid crystal line core, the mixture appears to be fairly heterogeneous in both crystalline and liquid crystalline states. The N–I transition shows non-linear features against the concentration of both components, though the mixture looks homogeneous in point of microscopy. Figure 3d shows the binary phase diagram for the mixture of *3f* and *4f*. As we can see from the figure, the mixture is heterogeneous in any state. Although the mixture at between 30 and 50°C

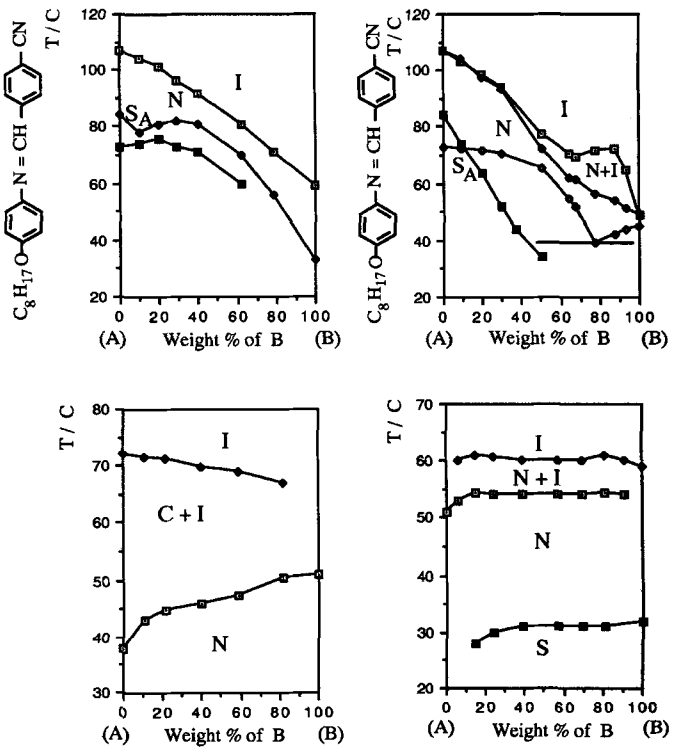


FIGURE 3 The binary phase diagrams for the mixtures of; (a) *N*-(4-cyanobenxylidene)-4′-octyloxyaniline (CBOOA)(on left) and *3f* (on right), (b) CBOOA (on left) and *4i* (on right), (c) the monomer of *4f* (on left) and *4f* (on right), (d) *4f* (on left) and *3f* (on right).

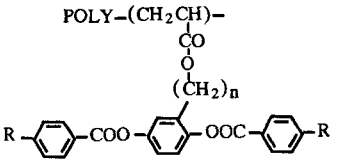
appears to be a homogeneous nematic phase in point of microscopy, the state would be a heterogeneous mixture of the nematic states of both components.

From these results, we can conclude that the liquid crystalline phases of polymers is fairly miscible with those of small molecules, but the miscibility becomes poor on increasing the molecular weight of the small molecules, and polar interactions tend to reduce the miscibility. The identification of the *S* phase is now underway.

The present results are compared with the thermal properties of related compounds hitherto reported in Table 4.

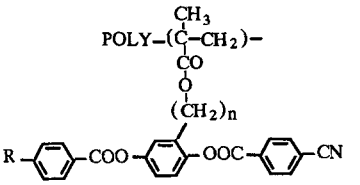
In spite of the difference in the structure of the main chain and position of the spacer group in the liquid crystalline core, compounds, *5*,[6] *6*,[5] *7*,[11] show similar mesomorphic properties to those of the present compounds. For example, polymers having the spacer group at the lateral position of the liquid crystalline core have difficulty in forming the smectic layer, have low melting points, and as a result are easily transformed into the glassy phase at the low temperature region. Compounds *8* having a spacer group at the longitudinal position of the liquid crystalline core have a stable smectic *C* phase and high melting points.[11] The structural characteristics are well reflected in the thermal properties of the laterally-attached liquid crystal polymers.

TABLE 4



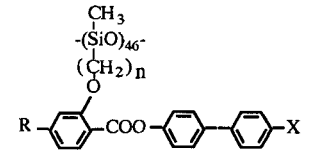
R = C_4H_9O, n = 11 G 4 N 67 I
R = $C_8H_{17}O$, n = 11 G -13 K 33 N 61 I

Compound 5



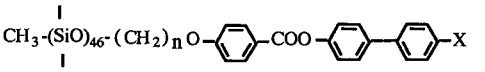
R = C_4H_9O, n = 11 G 36 N 76 I

Compound 6



R, X = $C_8H_{17}O$, n = 11 G -3.4 N 41 I
R = $C_{10}H_{21}O$,
X = $C_{10}H_{21}$, n = 11 G 3 N 37.3 I

Compound 7



X = $C_9H_{19}O$, n = 11 K 133.4 S_C 237.5 I

X = $C_{10}H_{21}$, n = 11 K 90.4 S 120 S_C 218.9 I

Compound 8

CONCLUSION

The present paper described the synthesis and thermal properties of novel polymer liquid crystals having a laterally-attached liquid crystalline core. These compounds preferentially show the nematic phase, and the smectic phase is observed only in the derivatives having long-spacer and terminal-alkoxyl groups. Interestingly, the two-ring compounds also form liquid crystalline phases when both terminal alkoxyl groups are sufficiently long. The cyano derivatives *4* have interesting dielectric properties and are useful for display devices.[17]

Acknowledgement

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References

1. H. Finkelmann, *Angew. Chem. Int. Ed. Engl.*, **26**, 816 (1987).
2. a) L. L. Chapoy (Ed.), "Recent Advances in Liquid Crystalline Polymers", Elsevier, Amsterdam, b) A. Blumstein (Ed.), "Polymer Liquid Crystals", Plenum Press, New York (1985).
3. F. Hessel and H. Finkelmann, *Polymer. Bull.*, **14**, 375 (1985).
4. F. Hessel and H. Finkelmann, *Polymer. Bull.*, **15**, 349 (1986).
5. F. Hessel, R.-P. Herr and H. Finkelmann, *Makromol. Chem.*, **188**, 1597 (1987).

6. F. Hessel and H. Finkelmann, *Makromol. Chem.*, **189**, 2275 (1988).
7. H. F. Leube and H. Finkelmann, *Makromol. Chem.*, **192**, 1317 (1991).
8. G. W. Gray, J. S. Hill and D. Lacy, *Angew. Chem. Adv. Mater.*, **101**, 1146 (1989).
9. M. K. S. Lee, G. W. Gray, D. Lacy and K. J. Toyne, *Makromol. Chem. Rapid. Commun.*, **10**, 325 (1989).
10. G. W. Gray, J. S. Hill and D. Lacy, *Mol. Crystl Liq. Cryst., Lett.*, **7**, 47 (1990).
11. G. W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **197**, 43 (1991).
12. T. Nakamura, T. Ueno and C. Tani, *Mol. Cryst. Liq. Cryst.*, **169**, 167 (1989).
13. S. Takenaka and K. Yamazaki, *Mol. Cryst. Liq. Cryst.*, in press.
14. S. Takenaka, H. Morita, M. Iwano, Y. Sakurai, T. Ikemoto and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **182B**, 325 (1990).
15. G. W. Gray and J. W. Goodby (ed.), "Smectic Liquid Crystals", Heyden & Son Inc., Philadelphia, 1984.
16. J. J. van Laar, *Arch. Neerl. Sci. Exactes. Natur.*, **118**, 264 (1903).
17. S. Takenaka and K. Yamazaki, to be published elsewhere.