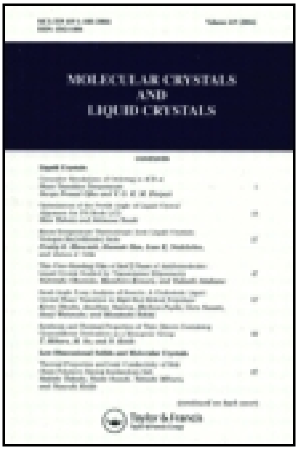

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Thermal Properties of Liquid Crystals Having an ω-Acryloxyoxyalkyl Group at the Lateral Position

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Thermal Properties of Liquid Crystals Having an ω-Acryloxyoxyalkyl Group at the Lateral Position

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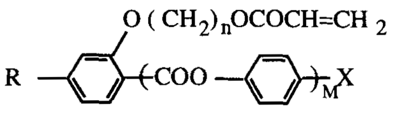
Some homologous members of 4-cyanophenyl and 4-alkoxyphenyl 4-(4-alkoxy-2-(ω-acryloyloxyalkoxy)benzoyloxy)benzoates, and 4-cyanophenyl and 4-alkoxyphenyl 4-alkoxy-2-(ω-acryloyloxyalkoxy)benzoates have been synthesized, and the thermal and dielectric properties have been investigated. Most members show a nematic phase while these have the bulky substituent at the lateral position. Even in two-ring compounds liquid crystalline phases are formed when both terminal alkoxy groups are suitably long. These compounds easily form glassy states corresponding to the liquid crystalline phases and the isotropic solution, where the relaxation process accompanies a remarkable change in the base line of the DSC thermogram. The thermal and dielectric properties are discussed in terms of the conformational and electrostatic properties of the ω-acryloyloxyalkoxy group.

Keywords: liquid crystals, mesomorphic properties, lateral substituent, dielectric properties, glassy transformation

INTRODUCTION

Generally, liquid crystals have a rod-like or a lath-shape molecular structure keeping rigidity and linearity. However, recent works have shown that some molecules having a long alkyl group at the lateral position frequently show liquid crystalline properties,[1-8] and the mesomorphism is strongly dependent on the position of the substituent.[1] In addition, we reported that some ester compounds having a 4-alkoxybenzoate group at the lateral position show nematic and smectic properties.[9,10] These facts indicate that the rod-like or the lath-shape is not an indispensable factor for displaying liquid crystalline properties, and a closed packing of these distorted molecules sometimes generates an orientational and/or a translational order, displaying the mesomorphic properties. Therefore, the binding position and shape of the lateral substituent are very important in determining the mesomorphism. In this connection, we are interested in the effect of the lateral substituent on the liquid crystalline properties, where the lateral alkoxy group involves an acryloyloxy group at the terminal position.



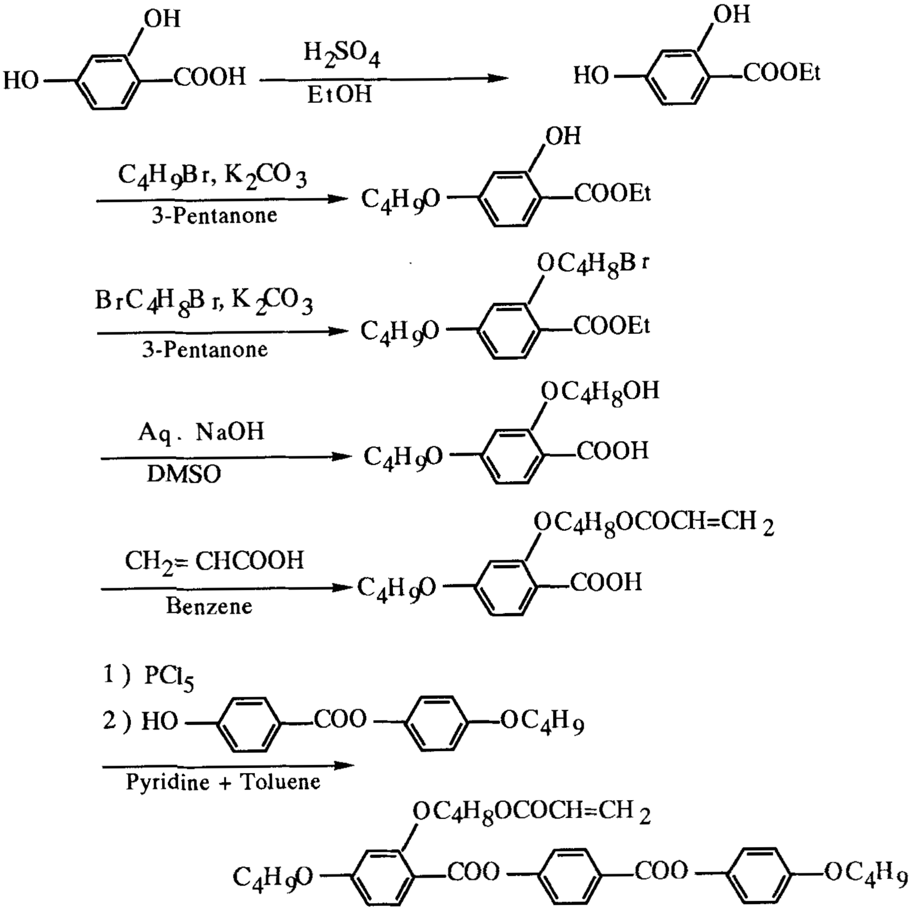
$R = C_mH_{2m+1}O \quad X = OC_mH_{2m+1}$ or CN $(m = 4, 8, 12)$

$n = 4, 5, 8, 12 \quad M = 1$ or 2

This paper describes synthesis, mesomorphic, and dielectric properties of these compounds, and the results will be discussed in terms of the molecular structure.

EXPERIMENTAL

4-(4-Butoxyphenoxycarbonyl)phenyl 2-(ω-acryloyloxybutoxy)-4-butoxybenzoate (3a) was prepared according to the following scheme.



SCHEME

Ethyl 2,4-dihydroxybenzoate: 2,4-Dihydroxybenzoic acid (15 g) in ethanol (300 ml) containing a few drops of conc. sulfuric acid was refluxed for 24 hrs, and most of the ethanol was removed by distillation. The residue was extracted with ether, and purified with column chromatography on silica-gel where benzene was used as a developing solvent, giving ethyl 2,4-dihydroxybenzoic acid as colorless needles (9.5 g). mp. 73°C.

Ethyl 4-butoxy-2-hydroxybenzoate; A 1:1 mixture of 1-bromobutane (47.6 g), anhydrous potassium carbonate (48 g), and ethyl 2,4-dihydroxybenzoate (66.6 g) in 3-pentanone (500 ml) was refluxed for 24 hrs. After removing the solid, the reaction mixture was concentrated and the residue was purified by column chromatography on silica-gel, where a mixed solvent of benzene and ether was used as a developing solvent, followed by recrystallization from pet. ether, giving ethyl 4-butoxy-2-hydroxybenzoate as colorless needles (72.2 g). mp. 51°C.

Ethyl 2-(ω-bromobutoxy)-4-butoxybenzoate; A mixture of ethyl 4-butoxy-2-hydroxybenzoate (20 g), 1,4-dibromobutane (76.9 g) and anhydrous potassium carbonate (11.6 g) in 3-pentanone (300 ml) was refluxed for 24 hrs. After removing the solid, the reaction mixture was concentrated to dryness. The residue was purified by column chromatography on silica-gel, giving ethyl 2-(ω-bromobutoxy)-4-butoxybenzoate as a colorless oil (26.3 g).

4-Butoxy-2-(ω-hydroxybutoxy)benzoic acid: A mixture of ethyl 2-(ω-bromobutoxy)-4-butoxybenzoate (26 g) in DMSO (100 ml) containing sodium hydroxide (10 g) and water (40 ml) was heated at 100°C for 3 hrs. The reaction mixture was extracted with chloroform, and the extract was dried over anhydrous sodium sulfate, and purified by column chromatography on silica-gel where a mixture of ether and benzene was used as a developing solvent, followed by recrystallization from a solvent mixture of ether and hexane, giving 4-butoxy-2-(ω-hydroxybutoxy)benzoic acid as colorless needles (8.6 g). mp. 103°C 2-(ω-Acryloyloxybutoxy)-4-butoxybenzoic acid: A mixture of 4-butoxy-2-(ω-hydroxybutoxy)benzoic acid (10 g), acrylic acid (10 g) *p*-toluenesulfonic acid (18 g), and 2,6-di-tert-butyl-4-cresole (7.7 g) in benzene (100 ml) was refluxed for 6 hrs where the water which formed was removed by the Dean-Stark apparatus. The reaction mixture was concentrated and extracted with ether. The extract was purified by column chromatography on silica-gel where a mixture of ether and benzene was used as a developing solvent, followed by recrystallization from a solvent mixture of hexane and ethanol, giving 2-(ω-acryloyloxy)-4-butoxybenzoic acid as colorless needles (5.3 g). mp. 50°C. 4-(4-Butoxyphenoxycarbonyl)phenyl 2-(ω-acryloyloxybutoxy)-4-butoxybenzoate (3a): 2-(ω-Acryloyloxybutoxy)-4-butoxybenzoyl chloride obtained by the reaction of 2-(ω-acryloyloxybutoxy)-4-butoxybenzoic acid (2.5 g) and phosphorous pentachloride, and 4-(4-butoxyphenoxycarbonyl)phenol (1.63 g) was reacted in a 1:1 mixture of toluene and pyridine (30 ml) at 80°C. After removing the solvent, the residue was extracted with ether. The extract was purified by column chromatography on silica-gel where a mixture of ether and benzene was used as a developing solvent, followed by recrystallization from a solvent mixture of ether and pet. ether, giving 3a (3.1 g). Anal. Found: C, 69.6; H, 6.66. Calcd. for $C_{35}H_{40}O_9$: C, 69.5; H, 6.67%.

The other compounds were prepared by a similar method. The identification of the products was carried out by elemental analysis and NMR.

Method: Phase transitions were observed by using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 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 a heating rate of 5°C (mp. 156.6°C, ΔH = 6.80 mcal/mg).

RESULTS

The transition temperatures and latent heats for compounds **1–4** are summarized in Tables I–III.

The transition temperatures and latent heats for the present compounds were determined by using a DSC thermogram. The typical example of the DSC thermogram for two-ring compounds is shown in Figure 1.

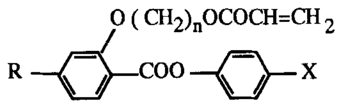
The DSC thermogram of compound 1a shows no peak on the cooling and heating stages. On the cooling stage of the isotropic solution, the thermogram shows only a remarkable change of the base line at −60°C, and −56°C on the heating stage. The change is a characteristic of a glass transition, and corresponds to the glassy state of the isotropic solution. A similar phenomenon is observed in the other derivatives of 1 and 2.

A similar phenomenon is observed in three-ring compounds **3–4**. An example is shown in Figure 2.

The DSC thermogram of the isotropic solution of compound 4a on the cooling stage shows an exotherm at 43°C due to the I-N transition as well as a remarkable change of the base line at −18°C. The enantiotropic change is observed on the heating stage, without recrystallization. Apparently, the remarkable change arises from the transformation process of the glassy state of the N phase. The glassy state is observed in most members. In two-ring compounds the relaxation temperature is in the range between −47 and −60°C. In three-ring compounds the relaxation

TABLE I

Transition temperatures (T/°C) and latent heats for

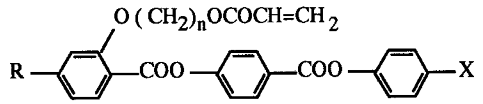


Compound	*R*	*X*	*n*	T_g	M^{*1}		*N*		*I*	Δ*H* (kJ/mol) *M-N*	Δ*H* (kJ/mol) *N-I*
1a	$C_5H_{11}O$	$C_5H_{11}O$	6	−56							
1b	$C_8H_{17}O$	$C_8H_{17}O$	12	−47	·	−28	·	−17	·	0.6	1.0
2a	$C_8H_{17}O$	CN	6	−55							
2b	$C_{12}H_{25}O$	CN	6	−55							
2c	$C_8H_{17}O$	CN	12	−58							

N and *I* indicate the nematic phase and isotropic solution, respectively. T_g indicates a glassy transition temperature. *1 probably, the smectic phase.

TABLE II

Transition temperatures (T/°C) and latent heats for

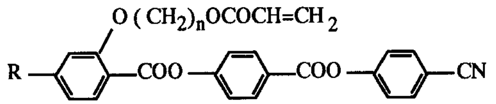


Compound	R	X	n	T_g	C		S_A		N		I	ΔH(kJ/mol) C-I	ΔH(kJ/mol) S_A-N	ΔH(kJ/mol) N-I
3a	C_4H_9O	C_4H_9O	4	−26	·	69	—		(·	48)	·	46.7		1.0
3b	C_4H_9O	C_4H_9O	6	−33	·	60	—		(·	41)	·	39.5		1.0
3c	C_4H_9O	C_4H_9O	12	−37	·	49	—		(·	36)	·	47.6		1.1
3d	$C_8H_{17}O$	$C_8H_{17}O$	4	−32	·	69	—		(·	39)	·	59.6		1.6
3e	$C_8H_{17}O$	$C_8H_{17}O$	6	−38	·	75	—		(·	37)	·	62.9		0.9
3f	$C_8H_{17}O$	$C_8H_{17}O$	12		·	60	—		(·	50)	·	78.8		1.7
3g	$C_{12}H_{25}O$	$C_{12}H_{25}O$	4		·	66	(·	44	·	60)	·	54.0	0.2	1.9
3h	$C_{12}H_{25}O$	$C_{12}H_{25}O$	6		·	71	(·	36	·	53)	·	81.3	0.2	1.5
3i	$C_{12}H_{25}O$	$C_{12}H_{25}O$	12		·	73	(·	35	·	51)	·	92.2	0.2	0.9

Parentheses indicate a monotropic transition. S_A indicates a smectic A phase.

TABLE III

Transition temperatures (T/°C) and latent heats for



Compound	R	n	T_g	C		N		I	ΔH (kJ/mol) C-I	ΔH (kJ/mol) N-I
4a	C_4H_9O	4	−16	·	75	(·	43)	·	23.0	0.5
4b	C_4H_9O	6	−22	·	73	(·	33)	·	35.6	0.4
4c	C_4H_9O	12	−31	·	45	(·	26)	·	47.4	0.5
4d	$C_8H_{17}O$	4	−25	·	61	(·	48)	·	38.5	0.9
4e	$C_8H_{17}O$	6	−29	·	67	(·	43)	·	55.9	0.7
4f	$C_8H_{17}O$	12		·	72	(·	38)	·	64.9	0.7
4g	$C_{12}H_{25}O$	4		·	76	(·	54)	·	47.2	0.9
4h	$C_{12}H_{25}O$	6		·	68	(·	46)	·	55.5	1.0
4i	$C_{12}H_{25}O$	12		·	60	(·	38)	·	44.1	1.5

Parentheses indicate a monotropic transition.

temperature is higher by 20–30°C than that of two-ring compounds. As we can see from the tables, the relaxation temperature of the cyano derivatives is higher than that of the alkoxy ones.

In two-ring compounds, liquid crystalline phases are formed only in 1b having long alkoxy groups at both terminal groups. Three-ring compounds 3 and 4 show an N phase, and some members having long alkoxy groups at both terminal positions show a smectic A phase (S_A) as well. The textures of both phases are shown in Figure 3.

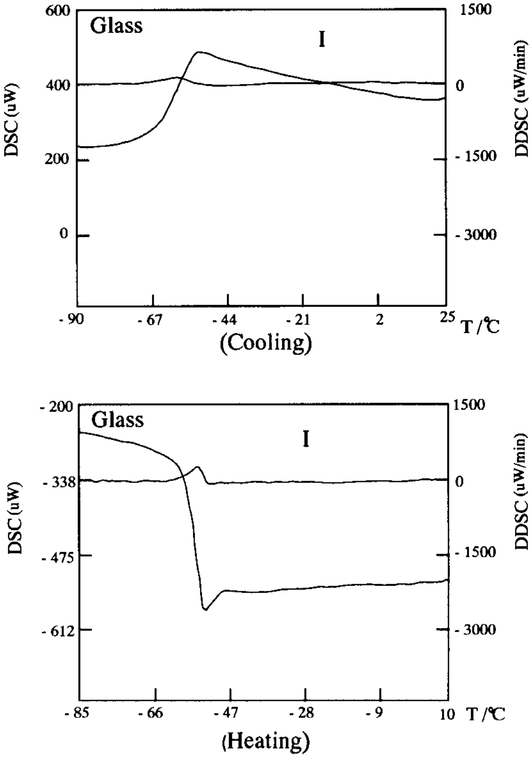


FIGURE 1 DSC thermograms of 1a. Heating and cooling rates of 5°C/min.

The N phase shows a schlieren texture with a complex birefringence (Figure 3-1). The S_A phase shows a somewhat interesting texture, as shown in Figure 3-2. The fans are fairly broken and have fine brushes.

The S_A phase was assigned from the examination of the miscibility diagrams for the mixture of these homologs and N-(4-cyanobenzylidene)-4-octyloxyaniline (CB00A), as shown in Figure 4.

In Figure 4-1 both the N-I and S_A-N transition show a little distortion from the straight line, where the S_A phase of CB00A is known to have a partially bilayer arrangement of the molecules.[11] In Figure 4-2 the mixture of 90% of CB00A and 10% of 4e shows no S_A phase, indicating that the formation of the S_A phase is difficult for 4e.

Dielectric properties of three-ring compounds are shown in Figure 5. All the compounds show positive dielectric anisotropy, where the anisotropies for compounds 3e, 3f, 4e, and 4f are 1.9, 2.3, 20, and 19 at T_{N-I} − 10°C), respectively.

DISCUSSION

In an earlier paper, we described the synthesis and thermal properties of 4-cyanophenyl 4-(2,4-dialkoxybenzoyloxy)benzoates.[1] In connection with the present work the thermal properties of the related compounds are shown in Table IV.

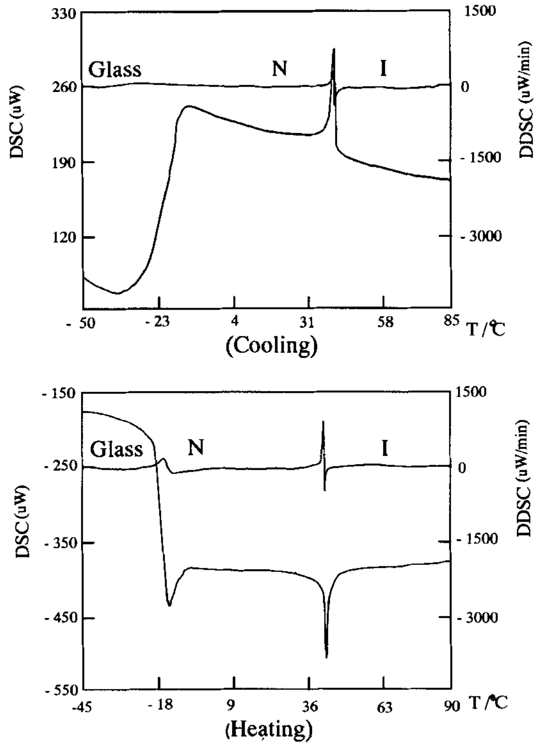
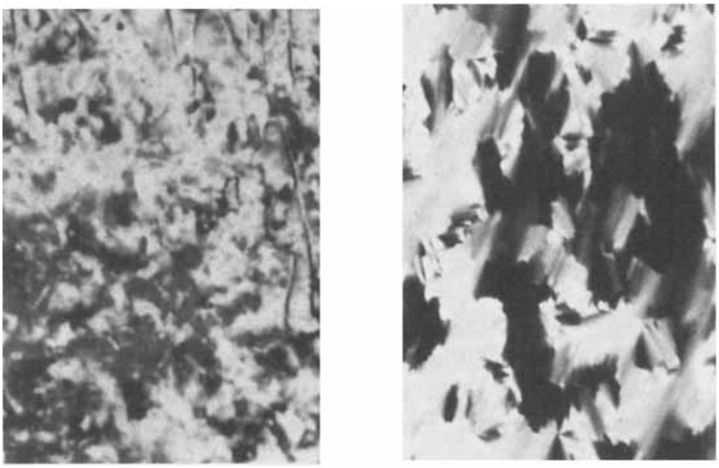
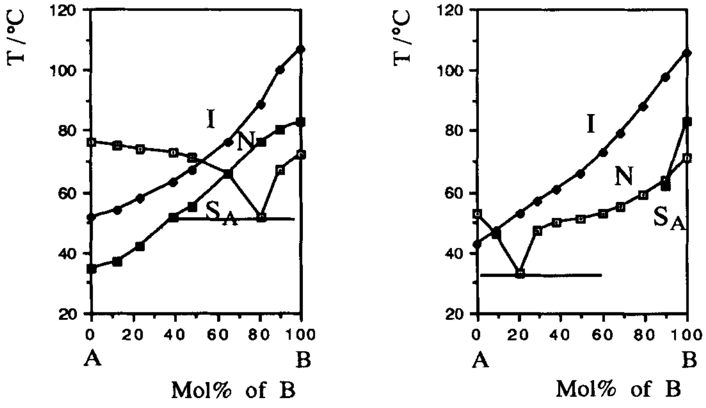


FIGURE 2 DSC thermograms of 4a. Heating and cooling rates of 5°C/min.



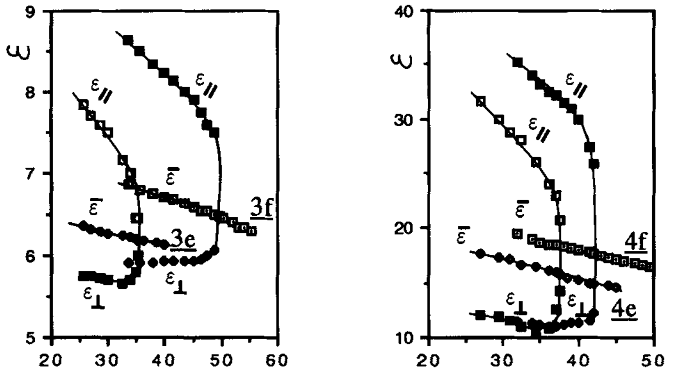
(1) (2)

FIGURE 3 Micrographs of 3i: (1) nematic phase, (2) smectic A phase. See Color Plate IX.



(1) (2)

FIGURE 4 Binary phase diagrams for the mixtures of (1) 3i(A) and CB00A(B), and (2) 4e(A) and CB00A(B).



(1) (2)

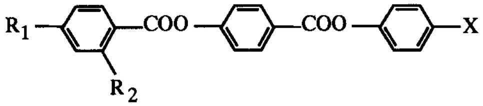
FIGURE 5 Temperature dependence of dielectric constants for (1) 3e and 3f, (2) 4e and 4f. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ indicate dielectric constants for longitudinal and transverse directions, and $\bar{\varepsilon}$ indicates the mean dielectric constant, $(\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$. The capacitor cell consisted of two indium-coated glass electrodes separated by a 25 μm spacer. The cell temperature was controlled by means of brass housing. The voltage applied was 0.4 V at 1 kHz. The alignment of molecules in the cell was achieved by applying a 1.0 *T* magnetic field. The capacitor cell was calibrated by highly purified acetonitrile.

Compounds 5 and 6 are considered to be typical "rod-like" liquid crystals. Higher members of compound 5 show the mesomorphic sequence of an S_C-S_A-N-I when $R_1 > X$, and S_C-N-I when $R_1 < X$, and the clearing point is high.[12] Compound 6 is a typical "polar" liquid crystal, and shows the reentrant sequence of an N_{re}-S_A-N-I when R_1 is suitably long.[13]

When hydrogen at R_2 is replaced by an alkoxy group, the thermal properties change remarkably, that is, the clearing points of 7 and 8 are lower by 150–200°C than those of 5 and 6, and the smectic phases disappear. The lateral alkoxy group would reduce the symmetry of the entire molecular structure, and the distortion

TABLE IV

Transition temperatures of compounds 5–8 (T/°C)



Compound	R_1	R_2	X	C		S_A		N		I	
5	$C_8H_{17}O$	H	$C_8H_{17}O$	·	84	·	163	·	188	·	*1
6	$C_8H_{17}O$	H	CN	·	123	·	158	·	233	·	*2
7	$C_9H_{19}O$	$C_9H_{19}O$	$C_9H_{19}O$	·	81	—		(·	67)	·	*3
8	$C_5H_{11}O$	$C_5H_{11}O$	CN	·	90	—		(·	60)	·	*3
	$C_8H_{17}O$	$C_8H_{17}O$	CN	·	68	—		(·	60	·	*3

*1An S_C-S_A transition occurs at 141°C (ref. 12). *2Ref. 13. *3Ref. 1.

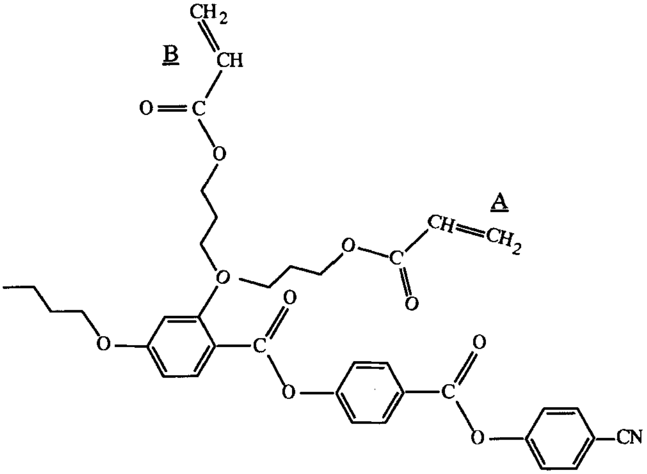


FIGURE 6 Possible conformations of compound 4a A and B indicate the conformations of the ω-acryloyloxybutoxy group at 2 position.

of the molecular structure may be responsible for the reduction of liquid crystalline properties.

The present compounds incorporate an acryloxyoxy group at the ω position of the lateral alkoxy group. The terminal group would increase the molecular breadth and reduce the liquid crystalline properties. Certainly, the clearing points of 3 and 4 are lower by 10–20°C than those of 7–8.

We mentioned in an earlier paper that the long substituent at 2 position for compound 7–8 reduces smectic properties probably due to intermolecular steric hindrance in the layer arrangement of the molecules.[1] A similar trend can be observed in compounds 1–4. The S_A phase having a monolayer arrangement of molecules is observed when both terminal alkoxy groups are sufficiently long. Some liquid crystals having an ω-vinylalkoxy group at the lateral position as the precursors corresponding to the polymers have been prepared, and are reported to show only a nematic phase.[14–20] In the earlier paper,[1] we assumed that the lateral long alkoxy group extends along the long axis of the core, for example, as shown in Figure 6 (A in the figure).

The conformational model appears to be reasonable for rod-like liquid crystals. A similar conformational model has been postulated by Weissflog *et al.*[5–7] for some liquid crystals having a lateral long alkyl group. In the conformational model, the ester group orients opposite to those within the core, so that the dipoles arising from the ester groups would some way cancel. Certainly, the dielectric anisotropies in the *N* phase for compounds 4e and 4f are smaller by ca. 10 than 8.[21]

As we can see from Tables I–III, most of the present compounds show a glassy phase corresponding to the states. Interestingly, the relaxation accompanies a remarkable change of the base line of the DSC thermograms. As far as the present compounds are concerned, the remarkable change is observed in the liquid crystalline phases and isotropic solution, and not in the solid phase. The relaxation temperature is affected not only by the size of the core but also by the length of the terminal alkoxy chains. The terminal cyano group also enhances the relaxation temperature.

A similar feature is observed in the DSC thermogram of the homologous series of 7.[22] The polymers of compounds 2–4 show a quite similar feature to the figures.[22]

From these results, we can conclude that the long alkoxy group at 2 position is concerned with the remarkable change of the base line. That is, the lateral alkoxy group would fairly rotate in the liquid crystalline phases and isotropic solution so that conformer B also plays some important roles for the liquid crystalline properties. The rotation would be fixed in the relaxation process, giving rise to change in the molecular volume. Further examination of the relaxation process is now in progress.

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