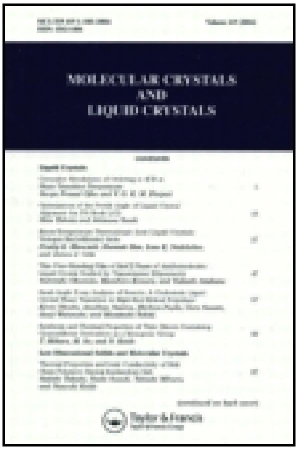

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A New Chiral LC Acrylate that Exhibits Pyroelectricity

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A New Chiral LC Acrylate that Exhibits Pyroelectricity

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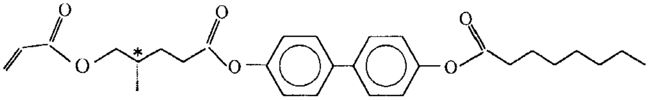
The new material (R)-4-(5-acryloyloxy-4-methylpentanoyloxy)-4′-octanoyloxy biphenyl has been synthesised and characterised by POM, DSC, X-ray diffraction, IR dichroism, pyro- and piezoelectric techniques. The acrylate was shown to exhibit direct isotropic to smectic H^* phase transition. The natural texture of the H^*phase separates from the isotropic phase in the form of bâtonnets and rounded domains, the latter develop into a mosaic. The mesophase was found to align in a thin cell of KBr plates with homeotropic anchoring independently of the type of surface treatment. The molecular organisation in the H^* phase strongly favours fast and efficient polymerisation when the initial orientation retains upon the reaction. The structure of the crystal and H^* phases is mono-layer, the molecules pack monoclinic in antiparallel fashion with long-range polar ordering. The pyroelectric coefficient was found to be very high in the crystal ($\gamma = 2.0 \div 2.9$ nC/cm^2·K) and H^*($\gamma = 2.9 \div 1.0$ nC/cm^2·K) phases. The direction of the macroscopic polarisation was not shown to be controlled by an external voltage. The piezocoefficient is stable and constant within the crystal phase ($d_{31} = 0.41$ nC/N).

Keywords: smectic H^* phase; textures; X-ray diffraction; surface induced alignment; pyroelectricity; piezoelectricity

INTRODUCTION

It had been known for a long time that when a tilted smectic phases, such as *C*, *F* and *I*, are composed of optically active molecules they usually exhibit a helical macrostructure based on the rotation of the tilt direction of individual layers about an axis normal to the layer planes on passing from layer to layer. In this case each layer has a net polarization in plane of the layer and no macroscopic polarization can be observed. However, it is possibly safe to say that in the case of higher ordered tilted smectics *J**, *G**, *H** and *K** the helical ordering can be suppressed by the long range positional correlations of the molecules[1], while keeping the in-plane polarizations unidirectionally arranged within crystallites or domains. On the other hand, the smectic *H* phase has been known to be exhibited by polymorphic compounds being separated from the isotropic phase by at least 2 - 3, less ordered mesophases[2]. This situation prevents from investigating natural behaviour of the mesophase in external fields.

In an attempt to examine the behaviour of directly formed smectic *H** phase we synthesized the acrylate, the (R)-4-(5-acryloyloxy-4-methylpentanoyloxy)-4'-octanoyloxy biphenyl



and investigated its structure, surface induced orientation and electric effects.

EXPERIMENTAL

The acrylate was prepared by standard methods as follows.

4-Hydroxy-4'-octanoyloxy biphenyl (**1**) was prepared by esterification of 4,4'-biphenyldiol with octanoyl chloride in the presence of pyridine. The esterification of **1** by (R)-5-Bromo-4-methylpentanoic acid[3] was carried out using standard method[4] to give (R)-4-(5-bromo-4-methylpentanoyloxy)-4'-octanoyloxy biphenyl (**2**) in good yield. The acrylate was obtained from **2** by nucleophilic substitution of lithium acrylate[5]. The crude product was purified by column chromatography using dichloromethane as eluant. Recrystallization from ethanol produced white crystals. $[\alpha]_D^{20}$ = +1.034° (c = 2.031g/dL in chloroform).

The phase assignments and corresponding transition temperatures were determined by polarised optical microscopy (POM) using a Leitz Ortholux Pol-BK microscope equipped with a Mettler FP52 hot stage, a Mettler FP5 temperature programmer, and a Wild Photoautomat MPS45 camera. Temperatures and enthalpies of transitions were investigated by DSC method using a Perkin-Elmer DSC-4 model and a Mettler TA 4000 system. Optical rotatory power was measured by means of a Perkin Elmer M-141 polarimeter in chloroform solution. The X-ray diffraction patterns of magnetically aligned samples (1.2 T) were recorded on flat photographic films and were taken with Ni-filtered CuK_α radiation. The temperature was controlled to ± 0.25°C by placing the sample in a microfurnace equipped with a temperature controlling unit. The X-ray photographs were scanned using a microdensitometric system (density scale 0-5) based on modified microphotometer MF-2 and a DP-1M densitometer. The values of the optical density were converted to X-ray intensity data following a standard procedure. The piezoelectric characterisation was carried out by the measurements of acoustically induced piezoelectric voltage[5]. The sample was placed into a 110 µm thick cell and cooled from the isotropic phase to room temperature at or without applied dc electric field. For pyroelectric measurements, a 100 µs pulse of a Nd^{3+} YAG laser (λ = 1.06 nm) was used to induce a heat increment in the electrooptic cell of 10 µm thickness with the applied bias dc voltage ranging from 0 to 30 V/µm. The sample preparation and the experimental set-up have been described elsewhere[6].

RESULTS AND DISCUSSION

DSC measurements

The first DSC heating trace, recorded on a virgin sample (solution grown crystals) shows two first order transitions, indicated by well resolved sharp peaks. The higher temperature peak is associated with a mesophase → isotropic transition, whereas that at lower temperatures is due to the fusion of a crystal phase. The formation of the latter phase upon cooling seems to be strongly inhibited. In fact, the relevant exotherm is affected by strong undercooling and is characterised by a very small enthalpy change. Upon reheating the fusion transition appears as a broad, multiple peak of low intensity, unless the measurements are spaced each other by no less than 24 h storage period at room temperature. The latter is illustrated by the data collected in Table I, where the result of the DSC measurements done on the same sample aged for period of 1 day to 1 year. As can be seen, the relevant temperature and the transition enthalpy for aged sample vary within acceptable limits and are lower than those recorded on the solution grown material. The latter may well be due to an appreciable difference in the size of crystalline domains which was verified by X-ray diffraction study described below. As for the higher temperature transition, the data in Table I show that the transition vary within acceptable limits

TABLE I Calorimetric data on the acrylate recorded in heating runs at 10°C/min after storage at room temperature for a different period.

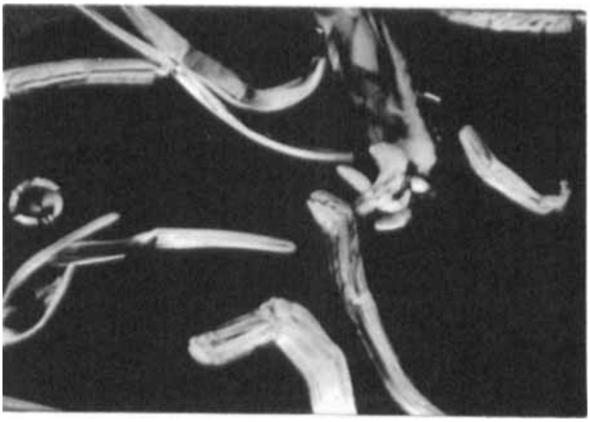
No. heating	Storage period, day	T_m °C	ΔH_m kJ · mol^{-1}	T_i °C	ΔH_i kJ · mol^{-1}
1	virgin sample	43.8	24.85	74.3	14.00
2	0	8.8; 18.2	6.30	73.8	12.10
3	363	33.2	7.40	73.8	11.73
4	13	32.2	7.35	72.9	11.20
5	4	31.2	7.64	72.9	11.10
6	1	30.7	7.59	73.5	11.34

upon rerunning independently of the thermal history of the sample.

POM observations

The POM analysis was done on a sample placed into a liquid crystal cell with twisted nematic polyimide coating. The isotropic → mesophase transition starts at ~70°C with the formation of typical bent bâtonnets (Fig. 1*a*) and is completed at ~65°C. The texture consists of brightly coloured, elongated domains and yellow-grey larger structures forming a mosaic shown in Fig. 1*b*.

(*a*)



(See Color Plate V at the back of this issue)

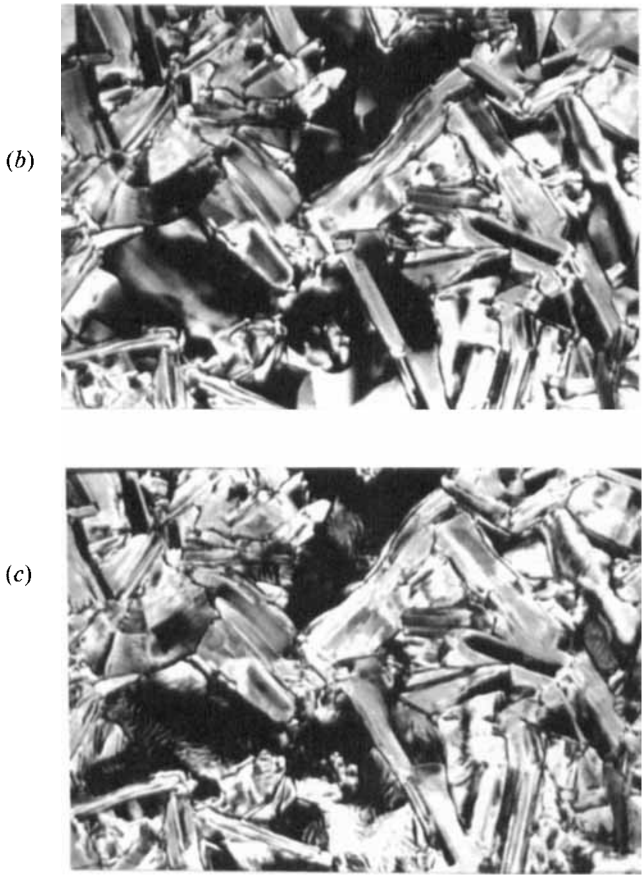


FIGURE 1 Photomicrographs of the smectic H^* phase observed on cooling from the isotropic phase at 69.4°C (*a*); 61.0°C (*b*), and on subsequent heating from room temperature to 54.5°C (*c*). The same area. Magnification: 320×. (See Color Plate V continued)

The temperature variations and, in particular, the subsequent heating from room temperature induce textural changes which are especially manifested by striations appearing in the larger domains. The effect becomes clearly visible at ~30°C and reaches a maximum at ~55°C (Fig. 1*c*). On further heating, the dark bands start fading at ~65°C and disappear completely in the 66 - 68°C range. Isotropisation starts at 68°C and ends at 72°C. Similar changes in the texture were observed on a sample placed between usual microscopic slides. The textures displayed by the mesophase are typical for an ordered smectic which was assigned by X-ray diffraction analysis as a smectic H^* phase.

X-ray diffraction data

By cooling the sample slowly from the isotropic phase to the mesophase in a magnetic field of 1.2 T it is possible to prepare rather good aligned specimen as shown by the diffraction pattern in Fig. 2*a*. On crystallisation the diffraction pattern of Fig. 2*b* is obtained which shows that the crystal layers retain the same orientation as the smectic layers.

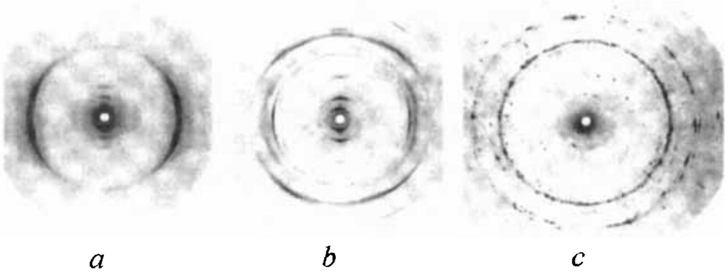


FIGURE 2 X-ray diffraction patterns obtained from magnetically aligned smectic H^* phase (*a*); from the crystal phase formed on cooling from the magnetically aligned smectic H^* phase (*b*), and from a solution grown crystals (*c*).

A powder diffraction pattern obtained from solution grown crystals is shown in Fig. 2*c*. It contains several Debey rings with numerous intense spots randomly distributed on them, thus showing that the specimen consists of fairly large crystalline domains. It should be noted that the both specimen give reflections being equal in spacings. This indicates that the compound crystallises from the mesophase in the same modification as from a solution while giving a fine-grained material.

The measured *d* spacings of the reflections of the crystal phase are collected in Table II. Taking into account these data and the molecular sizes, the first and second reflections may be associated with longitudinal molecular packing, whereas the third and forth reflections are certainly due to lateral packing. Since the first order spacing (27.9 Å) is shorter than the calculated length of the molecule in all *trans* conformation (l = 34.5 Å) a monolayer structure has to be considered including a tilt of the molecules in the layers. From this consideration, the X-ray reflections were indexed (Table II) using Ito's method[7]. These indices correspond to a monoclinic unit cell with the dimensions **a** = 34.4 Å, **b** = 9.90 Å, **c** = 10.70 Å, and γ = 125.7°. The unit cell contains four molecules provided their packing in antiparallel fashion as schematically shown in Fig. 3.1. The space group was determined as $P2_1$ in accordance with the absence of odd-numbered L in 00L reflections and with the symmetry of the molecule. This space group is well known to be characteristic of pyrocrystals.

The X-ray pattern from magnetically aligned mesophase at 20°C shown in Fig. 1*a* is characterised by four orders of Bragg reflections from the smectic layers, by two sharp crescents centered on the equator in the wide angle region and by two pairs of extra wide angle reflections situated on layer lines.

TABLE II The indexing of X-ray reflections of the crystal phase

No. reflection	d_{exp} Å	HKL	d_{calc} Å
1	27.90	100	27.90
2	14.15	200	13.95
3	8.03	010	8.03
4	5.37	002	5.37
5	4.87	$3\bar{2}1; 310; 5\bar{2}0; 7\bar{1}0$	4.84
6	4.42	$012; 3\bar{2}1; 311; 5\bar{2}1$	4.46
7	3.93	$212; 411; 6\bar{1}2$	3.90
8	3.73	021; 701	3.76
9	3.35	$1\bar{2}2; 1\bar{1}3; 2\bar{1}3; 220$	3.38
10	3.23	$022; 221; 4\bar{3}0; 702$	3.20
11	3.09	$3\bar{3}0; 320; 4\bar{3}1$	3.07
12	2.68	004; 023; 104	2.67
13	2.62	$031; 2\bar{3}2; 2\bar{1}4; 204$	2.59

The small angle reflections give the smectic period of d_M = 30.6 Å at 20°C which retains almost constant upto ~65°C. Since the measured layer spacing is shorter than that estimated assuming a fully extended molecular length, a monolayer structure can be considered including a tilt of the molecules in the layer to be of $\theta_{\text{X-ray}} = 27°$. The layers are aligned normal to the magnetic field direction with the orientation parameter **P** = 0.84. There is a good correlation between layers amounting to above 4 layers (the correlation length is of ~135 Å).

The sharp wide angle crescents centered on the equator correspond to a repeat distance d_E = 4.59 Å at 20°C and are associated with a rather good positional correlation of the molecules within the layer extending over about 20 molecules (the correlation length is of ~88 Å).

The extra wide angle reflections situated on the layer lines (d_L = 4.43 Å and 4.03 Å) can be interpreted in terms of a space lattice. Thus, the diffraction pattern obtained from the mesophase is identical to that from three dimensional smectic H^* phase[8].

The described diffraction features of the H^* phase index in terms of monoclinic unit cell taking into account axial macroscopic symmetry of the sample aligned by the magnetic field. The unit cell with the dimensions **a** = 34.5 Å, **b** = 9.1 Å, **c** = 5.0 Å and β = 117° contains two molecules. The space group was determined as $P2_1$ in accordance with the absence of odd-numbered K in 0K0 reflections and with the symmetry of the molecule. Like the crystal phase, the antiparallel molecular packing and polar ordering maintain in the H^* phase as shown schematically in Fig. 3.2.

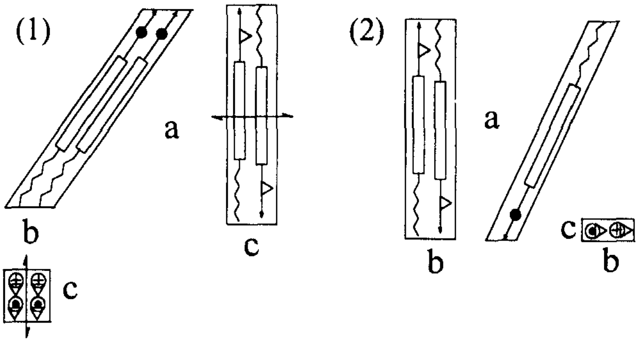


FIGURE 3 Packing arrangement of the molecules in the unit cell of the crystal (1) and smectic H^* (2) phases.

Orientation behaviour

The orientation of the acrylate in the H^* phase was examined using the transmission IR spectroscopy. A sample was placed between two KBr plates in the isotropic phase and then was cooled to the mesophase at a rate of 0.1°C/min. The inner surfaces of the plates were polished either on a Cr_2O_3 powder unidirectionally or on that with adding ethanol uniformly. The procedure of repeated heating and cooling was adopted to obtain a better sample alignment, and was accompanied by monitoring the vinyl C-H bending at 1408 cm^{-1} with the vibration at 1500 cm^{-1} as an internal reference. No change in the intensity of the bending vibration was observed indicating that the polymerisation of the acrylate was not thermally initiated.

The molecules of the acrylate were found to have tendency to homeotropic anchoring independent of the type of surface treatment. Thus, the orientation parameter, **P**, was determined using unpolarized IR radiation and by comparing the IR spectrum of the acrylate in the mesophase with that of the isotropic phase. In this case, the **P** value was estimated from relative band intensity of two vibrations with parallel (aromatic C-C stretching at 1500 cm^{-1}) and perpendicular (aromatic C-H out-of-plane vibration at 840 cm^{-1}) direction of transition moment with respect to the long axis of the biphenyl core[9] according to the expression

$$\mathbf{P} = (R - 1)/(R + 0.5) = 1 - 1.5\,\langle \sin^2\theta \rangle \qquad (1)$$

where R is dichroic ratio which for unpolarised beam is defined as follows

$$R = (D^{t}_{840} \times D^{iso}_{1500}) / (D^{t}_{1500} \times D^{iso}_{840})$$

where D^t and D^{iso} are the optical densities of the bands at the measuring temperature and those of the isotropic phase, respectively; θ - is the angle between the long axis of the biphenyl core and the normal to the substrate (the direction of the incident IR beam).

The plot of the orientation parameter as function of temperature is presented in Figure 5. The maximum value of **P** is found to be 0.69 over a wide temperature range of the *H** phase. The change in the relative intensity of the bands indicates that the long axis of the biphenyl core in the mesophase is tilted by $\theta_{IR} = 27°$ from the homeotropic direction, extracted from the expression (1). The θ value is in perfect agreement with the correlated tilt of the molecules within the layer evaluated from the X-ray data. This indicates that the long axis of the molecule as whole coincides well with that of the mesogenic core. The acrylate was shown to undergo photopolymerisation in the *H** phase when exposed to UV irradiation. The polymerisation of 10 μm thin film of the acrylate placed between two KBr plates was carried out by direct photolysis for 60 s at 50°C from a 280 W medium pressure mercury lamp. The absorption bands responsible for

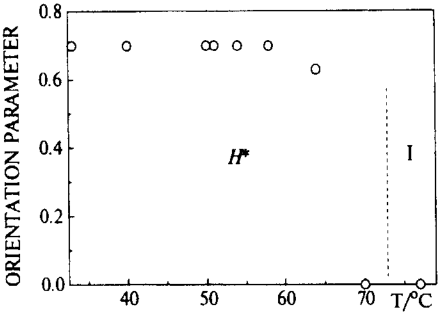


FIGURE 5 Variation of the orientation parameter, **P**, as function of temperature for the smectic *H** phase.

the vibration of the acrylic group completely vanished indicating that the degree of conversion is of 100%. The macroscopic orientation of the polymeric film obtained was found to be unchanged.

Pyroelectric and piezoelectric measurements

The acrylate was found to exhibit pyroelectric behaviour both in the crystal and *H** phases. When the sample is prepared by cooling from the isotropic phase, a stable pyroelectric response is observed in the crystalline phase. The polar state appears spontaneously and is not driven by an external dc bias voltage. The variation of the pyroelectric coefficient, γ, as function of temperature is shown in Fig. 6 in heating run without applying bias voltage. As can be seen, the γ (T) curve has a rather sharp maximum at 35°C which coincides well with the crystal - *H** phase transition temperature detected by DSC measurement. The pyroelectric response abruptly drops to zero at the transition into the isotropic phase. The above findings indicate that both the phases behave like pyroelectric material. It should be noted that the γ value measured on the fine-grained sample is very high ($\gamma = 2.0 \div 2.9\ \mathrm{nC/cm^2 \cdot K}$) and may approach a much higher value in a single crystal specimen. However, the photopolymerisation of the acrylate in the *H** phase was found to be accompanied by a collapse of the pyroelectricity in the polymeric film produced.

As pyroelectric material, the acrylate displays a fairly strong piezoelectric effect. It is observed in both the phases independently of whether or not the

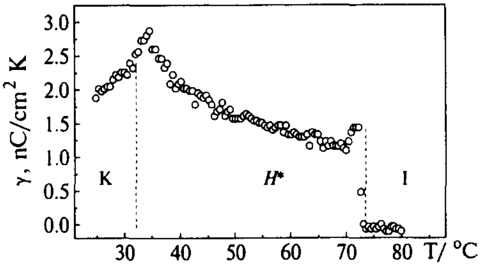


FIGURE 6 Pyroelectric coefficient, γ, versus temperature for the acrylate (the dashed lines denote the transition temperatures measured by DSC method).

sample was poled during cooling from the isotropic phase. In addition, any cycle (poling voltage positive and then negative) was not observed over all temperature range of the measurement. Figure 7 presents the variation of the

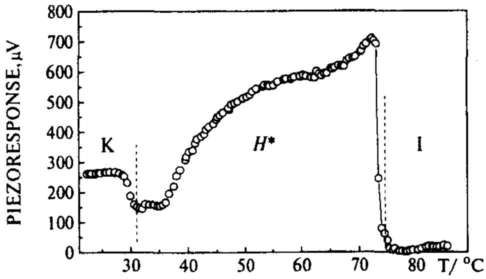


FIGURE 7 Piezoelectric response versus temperature for the acrylate.

piezoelectric response with temperature. The piezocoefficient was found to be stable and constant within the crystalline phase (d_{31} = 0.41 nC/N) and increases within the *H** phase as the temperature increased achieving d_{31}=1.1 nC/N some 2°C before the isotropisation.

CONCLUSIONS

The acrylate under study proved to be unique in some properties. It exhibits direct isotropic → smectic H^* phase transition showing its natural microscopic texture. The molecules in the H^* phase have a tendency to homeotropic anchoring on the KBr surface independently of the type of the surface treatment. The molecular organization in the smectic H^* phase strongly favor fast and efficient polymerisation when the initial homeotropic orientation retains upon the reaction. The acrylate proved to be a rare case of pyroelectric material being observed in organic compounds.

Acknowledgments

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