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Synthesis and characterization of new chiral mesogenic monomers

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New mesogenic monomers carrying substituted biphenyl rings linked to acryloyl or methacryloyl moieties through straight or chiral flexible spacers have been synthesized. All the investigated monomers, independent of the side group chirality, have been found to form ordered smectic phases, most probably of the S_1 type. The asymmetric methyl substitution on the flexible spacer leads to an expansion of the temperature range of mesophase stability. The chiral monomers induce a helical structure when mixed with appropriate nematogens. The fingerprint texture of a contact mixture of the chiral methacrylate prepared in this work, with a nematic methacrylate synthesized previously, has been found not to change after UV-initiated polymerization.

1. Introduction

Mesogenic compounds containing asymmetric carbon atoms are commonly used as chiral nematic phases and ferroelectric liquid crystals, and also as dopants, to induce a helical structure in nematics or tilted smectics. Chiral mesogens containing a polymerizable group are of great interest because their photopolymerization, in the form of oriented sandwiched samples [1], can result in new polymeric materials having unique properties [2].

In this respect, a new approach to polymer design suggested by Scherowsky and coworkers [3] deserves attention, this consists of the introduction of a chiral centre on the flexible spacer linking the mesogenic group to the backbone. Restricted motion of the chiral centre may in fact lead to an additional favourable effect in liquid crystal side chain polymers. Accordingly, the study of the mesogenic properties of monomers containing a chiral branched spacer unit is of interest, in view of the preparation of liquid-crystalline side chain polymers of a novel type. This paper describes the synthesis and the mesomorphic behaviour of four new monomers with acrylate and methacrylate groups, separated from the mesogenic core either by straight or chiral branched spacer units.

2. Experimental

2.1. Materials

5-Bromopentanoic acid (1) was purchased from Fluka and used as received. Other ordinary compounds and solvents were also of commercial source, unless otherwise stated.

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(*R*)-Tetrahydro-5-methyl-2H-pyran-2-one (**2**) was synthesized according to a literature method [4–6]. The compound was purified by fractional distillation in vacuum. The fraction boiling at 55–60°C/0.5 mbar was collected and kept in a refrigerator, before being used, so as to avoid any loss of product due to spontaneous polymerization. $[\alpha]_D^{20} = +14.7^\circ$ (CHCl₃).

(*R*)-5-Bromo-4-methyl-pentanoic acid (**3**) was prepared by reaction of the chiral lactone **2** with gaseous HBr in distilled water, at 0°C. After complete absorption of HBr, the mixture was heated on a water bath for 1 h. The product was extracted five times with diethyl ether. The combined extracts were dried over sodium sulphate. The solvent was evaporated and the liquid residue distilled in vacuum to give pure **3**: yield 60 per cent; bp 103°C/0.5 mbar; $[\alpha]_D^{17} = +3.8^\circ$ (CHCl₃).

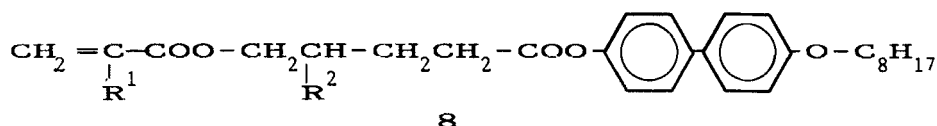
4-Hydroxy-4'-octyloxybiphenyl (**4**) was prepared from equimolar amounts of 4,4'-dihydroxybiphenyl and 1-bromooctane, with a trace of KI, in absolute ethanol. To this mixture, an equivalent amount of potassium ethoxide in ethanol was added under reflux, over a 1 h period. The reaction mixture was then cooled to room temperature and poured into water: the white precipitate was washed repeatedly with warm water (70°C), and dried. Extraction with boiling petroleum ether and the subsequent evaporation of the solvent led to a solid which was treated with methanol. Pure **4** was obtained as a clear solution in methanol (yield 35 per cent); the concomitant disubstituted compound was separated as a solid, due to its lower solubility.

(*R*)-4-(5-Bromo-4-methyl-pentanoyloxy)-4'-octyloxybiphenyl (**5**) was obtained by direct esterification of **3** with **4**, according to the procedure described by Hassner and Alexanian for the synthesis of halogenated alkoxyphenyl-(alkanoyloxy)-benzoates [7]; yield 98 per cent; $[\alpha]_D^{19} = +5.3^\circ$ (CHCl₃).

Sodium acrylate (**6**) and sodium methacrylate (**7**) were prepared by neutralization of the corresponding acids with NaOH, using routine laboratory methods.

2.2. Monomer synthesis

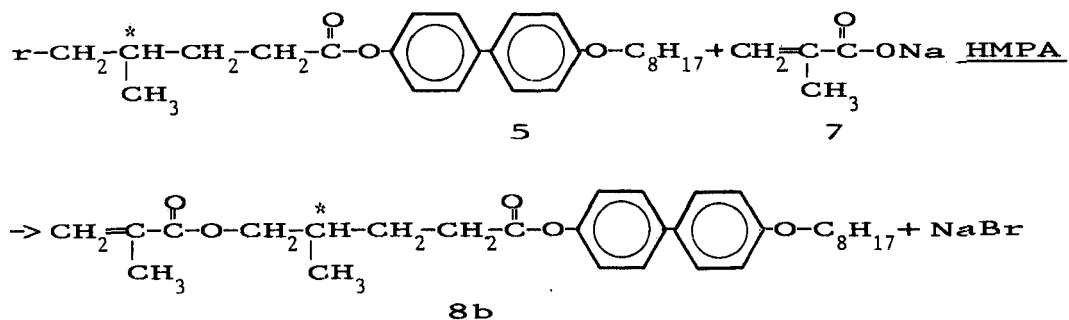
The synthesized mesogenic monomers are acrylates and methacrylates having the following general formula. They will be referred to, hereafter, as **8a–d**.



	R ¹	R ²
8a	H	CH ₃
8b	CH ₃	CH ₃
8c	H	H
8d	CH ₃	H

The monomers were prepared by reaction of **6** or **7** with the appropriate bromopentanoic acid derivative, using the procedure described by Shaw *et al.* [8].

The synthesis of **8b** is described as an example.



A mixture of 0.7 g (1.5 mmol) of **5** and 0.4 g (3.0 mmol) of **7** in 10 ml of hexamethylphosphoramide (HPMA) was stirred for 6 h at room temperature. The reaction mixture was then poured into ice water and the precipitate was collected on a sintered glass filter. The crude product was dried in vacuum and purified by column chromatography on silica gel, using dichloromethane as the eluant; yield 53 per cent. **8a**: $[\alpha]_{\text{D}}^{17} = -1.1^\circ (\text{CHCl}_3)$; **8b**: $[\alpha]_{\text{D}}^{16} = -3.4^\circ (\text{CHCl}_3)$.

2.3. Characterization methods

The purity of the reaction products was checked by size exclusion chromatography using a chromatograph (Millipore–Waters) equipped with dual detection and ultra-styragel columns (100 Å pore size), and using tetrahydrofuran as eluant.

The structural identification of monomers and intermediates was done by ^1H NMR, ^{13}C NMR and IR spectroscopy. Typical ^1H NMR (CDCl_3) data for monomer **8a** are as follows: $[\delta$ 7.58 (d, 2H), 7.50 (d, 2H), 7.17 (d, 2H), 6.95 (d, 2H), aromatic protons], [6.40 (2d, 1H), 6.10 (2d, 1H), 5.81 (2d, 1H), vinyl protons], 4.03 (t, 2H, CH_2O), 3.45 (d, 2H, CH_2OCO) 1.93–2.06 (m, 2H, methylene group), 1.82 (t, 2H, CH_2COO), 1.70–1.86 (m, 1H, methyne group), 1.26–1.50 (m, 12H, methylene groups), 1.13 (d, 3H, methyl group), 0.93 (t, 3H, methyl group).

The birefringent textures of monomers **8a–d** were observed with a polarizing microscope (Boetius) equipped with a hot stage. Their thermal behaviour was examined by differential scanning calorimetry (DSC-4, Perkin–Elmer), using a scan rate of 10 K min^{-1} . The X-ray patterns were taken on a URS-2.00 instrument, using nickel filtered Cu-K_α radiation. The measurements were made with a URK-3 camera equipped with a hot stage. The liquid-crystalline samples were oriented with a magnetic field of 1.4 T during their cooling from the isotropic melt.

3. Results and discussion

The microscopic textures of **8a–d** are shown in figure 1. All textures are typical of smectic phases.

Only the clearing point of these monomers could be detected by optical methods during their heating on the hot stage: the melting point could not be seen with this technique, due, probably, to paramorphosis. Upon cooling, a remarkable supercooling effect was observed for all monomers at the C–S transition. Its extent was found to vary with the cooling rate, but it was particularly prominent for the chiral compounds. It should be noted that the sandwich type samples (about $10 \mu\text{m}$ thick) were not oriented homeotropically in the mesophase by means of a surfactant.

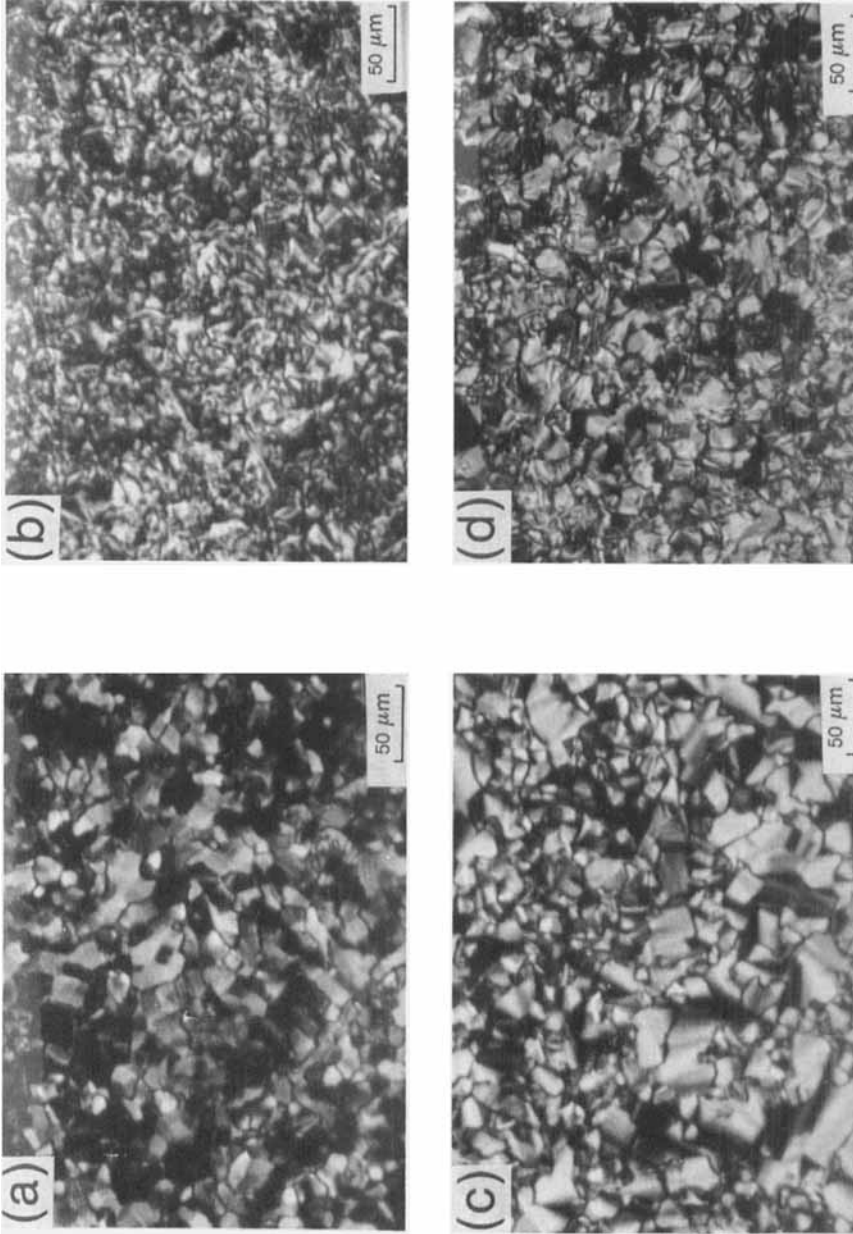


Figure 1. Micrographs of the mesophase textures (a) **8a**, (b) **8b**, (c) **8c**, (d) **8d**.

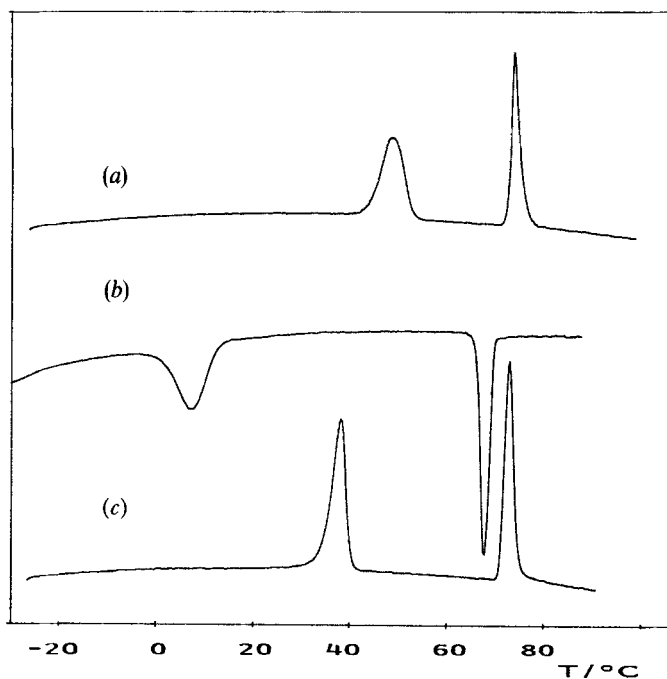


Figure 2. DSC traces of **8a**. (a) First heating, (b) cooling, (c) second heating. Scan rate = 10 K min⁻¹.

Table 1. Calorimetric data for monomers **8a-d**.

Monomer	DSC scan†	C-S transition			S-I transition			ΔT °C
		T °C	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹	T °C	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹	
8a	I	48.7	15.75	48.90	73.9	12.62	36.35	25.2
	II	4.5	10.41	37.09	67.8	10.94	32.08	63.3
	III	38.2	12.41	39.96	72.9	11.00	31.77	34.7
8b	I	46.0	17.55	54.97	64.1	10.32	30.58	18.1
	II	-4.7	9.10	33.86	57.7	9.66	29.18	62.4
	III	31.9	13.30	43.73	62.8	10.12	30.12	30.9
8c	I	84.1	18.55	51.91	91.7	11.12	30.47	7.6
	II	53.5	18.99	58.10	86.3	13.19	36.68	32.8
	III	80.4	19.44	54.97	91.0	12.92	35.47	10.6
8d	I	80.6	16.45	46.48	86.2	8.48	23.59	5.6
	II	43.7	15.53	49.00	82.0	11.94	33.59	38.3
	III	76.5	18.79	53.73	85.9	10.92	30.40	9.4

† I, first heating; II, cooling; III, second heating. Scan rate = 10 K min⁻¹.

The DSC curves of the monomers are characterized by two endothermic peaks on heating and two exothermic peaks on cooling. As an example, the DSC traces of the chiral acrylic monomer **8a** are shown in figure 2. The calorimetric data for **8a–d** are collected in table 1. As it is clearly seen from this table, different figures for the melting temperatures of all the monomers investigated were recorded on the first and the second heating scans. This might be due to some difference of crystal habit between the virgin samples and those crystallized by cooling from the melt. It is worth noting that the measured isotropization enthalpies are relatively high (50 to 80 per cent of the corresponding melting enthalpies), and this is typical for mesophases of comparatively high order.

It may also be observed that the presence of a methyl substituent, in the methylene spacer, leads to a lowering of the clearing temperature and to a considerably more pronounced depression of the melting point. Thus, the presence of a chiral centre at the γ position of the spacer results in an expansion of the mesophase range, as measured on the second heating scans, from *ca.* 10 to over 30 K. In contrast to this, the known mesogens containing the chiral centre within the terminal groups exhibit narrower mesophase ranges with respect to the corresponding achiral compounds [9, 10].

The replacement of the α hydrogen of the vinyl group by a methyl group leads to a slight depression of the transition temperatures.

The optical observation, as well as the DSC measurements indicate that all of the monomers investigated are monomorphic, i.e. they display single mesophase behaviour.

The X-ray diffraction patterns of the smectic phases, oriented in a magnetic field, are shown in figure 3. It is evident that the chiral compounds are much better oriented than the achiral ones. The small angle meridional reflection corresponds to the layer spacing d , while the wide angle sharp reflection is characteristic of the intermolecular distances. The parameters of the smectic structures are summarized in table 2. The average intermolecular distance D was calculated from $2D \sin \theta = 1.1547 \lambda$, on the assumption of an hexagonal lattice [11]. For all monomers but **8b**, the layer thickness d is less than the molecular length (34.2 Å) calculated from standard bond lengths and angles, with the assumption of a planar, all *trans* conformation of the molecule. This indicates that the long axes of their molecules are tilted with respect to the layer normal.

According to the optical observations and the DSC and X-ray data, all of these monomers display an ordered, tilted smectic phase, presumably of the S_1 type. This conclusion is based on the following considerations:

- (i) among ordered mesophases, only S_E , S_B and S_1 phases are monomorphic [12];
- (ii) the mosaic texture of the S_1 phase never transforms into a fan shaped or a homeotropic texture [13];
- (iii) the X-ray pattern of the S_1 phase is characterized by a sharp inner ring and a sharp outer ring, the d spacing of the inner ring is not coincident with the length of the molecule [13].

In the particular case of monomer **8b**, the difference between the layer thickness and the molecular length (33.5 versus 34.2 Å) is actually within the expected experimental error. Therefore, for this monomer, a smectic mesophase with untilted molecules (S_B) cannot be ruled out with certainty. A more detailed discussion of the smectic structure of the investigated monomers will be reported in a forthcoming paper.

The chiral monomers **8a** and **8b** were used as dopants and were found to induce a helical structure in appropriate nematogens. The textures presented in figure 4 were

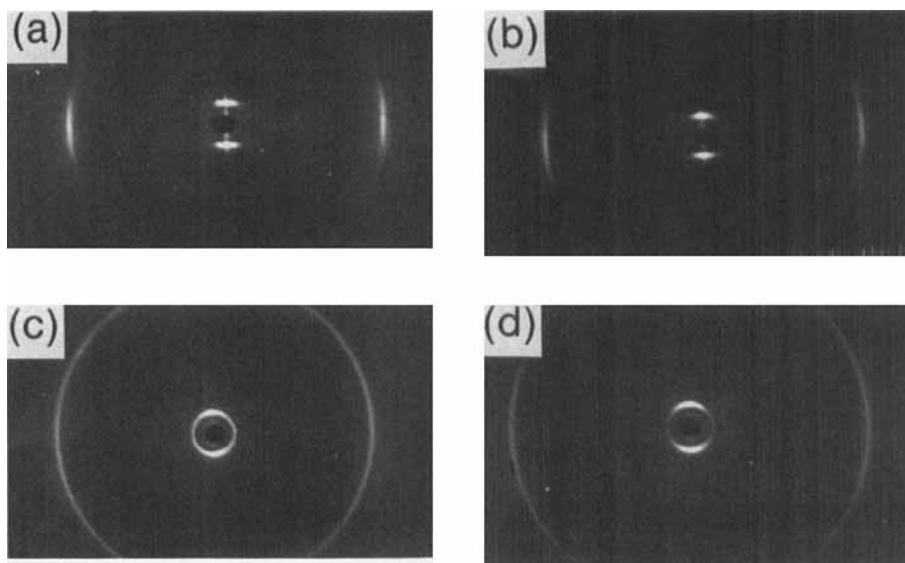


Figure 3. X-ray diffraction patterns of the mesophases oriented in a magnetic field. (a) **8a**, (b) **8b**, (c) **8c**, (d) **8d**.

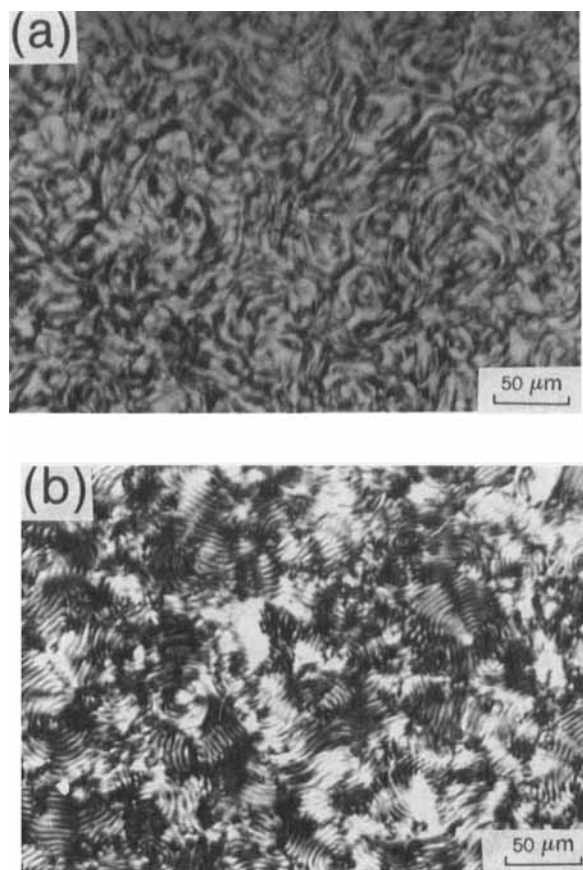


Figure 4. Micrographs of the contact mixture of **8b** and **M-06**. (a) Focal conic texture, (b) fingerprint texture. $T = 55^{\circ}\text{C}$; yellow filter, $\lambda = 620\text{ nm}$.

Table 2. Layer spacing d and intermolecular distance D of monomers **8a-d**, oriented in a magnetic field.

Monomer	T °C	d Å	D Å
8a	60	31.1	5.12
8b	57	33.5	5.27
8c	80	31.5	5.09
8d	77	28.7	4.61

observed with a contact mixture of **8b** and 4-methacryloyloxyphenyl-4'-hexyloxybenzoate (**M-06**) [14] in the nematic phase. The pitch was obtained from double the spacing of the stripes of the fingerprint texture (see figure 4(b)); the twist angle θ_p was calculated from $\theta_p = 2\pi d/p$. The pitch was found to be $6\ \mu\text{m}$, and the twist angle was calculated as 0.03° under the assumption that the average spacing of the adjacent pseudo-nematic layers is about $5\ \text{Å}$ [11]. Thus, no selective reflection of visible light can be expected.

The polymerization of this contact mixture, initiated by UV irradiation, leads to a disturbance of the focal conic texture, while the fingerprint texture and, consequently, the parameters of the helical structure remain unchanged. We could not find any previous report, in the literature, of such a frozen-in fingerprint texture obtained by UV polymerization. This last method can be expected to be successful in producing diffraction gratings of phase type with a sine law distribution of optical density [15].

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