# Helical pitch of ferroelectric liquid-crystalline polymers and copolymers

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# Helical pitch of ferroelectric liquid-crystalline polymers and copolymers

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Ferroelectric liquid-crystalline polymers and copolymers were synthesized from acrylate polymers with side chains consisting of a flexible spacer unit, a mesogenic unit and an optically active substituent. In the chiral smectic C ($S_C^*$) phases typical fan-shaped textures with equidistant lines (caused by the helical structures) were observed. It was found that the helical pitch increased with increasing polymer molecular weight. The helical pitch also increased in copolymers containing mixtures of right- and left-handed chiral side chains.

## 1. Introduction

In recent years ferroelectric liquid-crystalline polymers (FLCPs) have been extensively studied [1–5]. We have already discussed the ferroelectricity of our synthesized FLCPs [6]. We measured the layer spacing of the FLCPs using the small angle X-ray diffraction method and identified tilted smectic phases. We also identified the ferroelectricity by measuring the spontaneous polarization.

In the present study we observed the typical fan-shaped texture with equidistant lines caused by a helical structure. Helical pitch is one of the important physical parameters because it is related to the surface stabilized bistable effect. Firstly, we measured the helical pitch of FLCPs having the same molecular structure and different molecular weight.

The helical pitch of low molar mass ferroelectric liquid crystals can be expanded (compensated) by mixing right- and left-handed chiral smectic liquid crystals [7, 8]. We adopted this method for the expansion of the helical pitch in the FLCPs. In our survey, this is the first reported case of ferroelectricity in liquid-crystalline copolymers. We synthesized copolymers which have randomly right- and left-handed chiral parts in their side chains. We measured the helical pitch of these copolymers and investigated the relation between helical pitch and composition of copolymers.

## 2. Experimental

The polymer FLCP a1 was synthesized as follows. Acrylic acid (0·20 mol, 14·1 g), tetramethylammonium hydroxide pentahydrate (0·22 mol, 40·0 g), and 1,12-dibromo-dodecane (0·60 mol, 197 g) were reacted for 10 h in 300 ml of DMF. The reaction solution was ether extracted after the addition of 300 ml of water, then purified by column chromatography to yield 47·9 g of the objective bromoester compound (1).
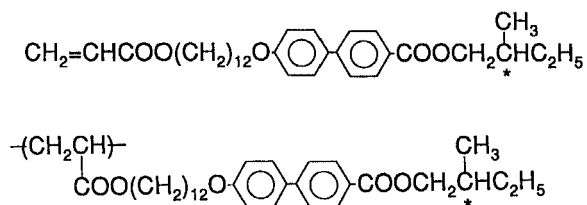
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$$CH_2{=}CHCOO(CH_2)_{12}O\langle\bigcirc\rangle\langle\bigcirc\rangle COOCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$$

$$-(CH_2\overset{|}{C}H)-\\ \overset{|}{C}OO(CH_2)_{12}O\langle\bigcirc\rangle\langle\bigcirc\rangle COOCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$$

Figure 1.    Molecular structures of the monomer (a) and the polymer FLCP a1.

4'-Hydroxybiphenyl-4-carboxylic acid (0·093 mol, 20·0 g) and (S)-(−)-2-methylbutanol (0·47 mol, 41·0 g) were then refluxed for 25 hours in 150 ml of benzene in the presence of 2 ml of conc. sulphuric acid. The reaction solution was next concentrated, and then recrystallized from a toluene hexane mixture to yield 26·0 g of hydroxyester compound (2).

A mixture of the bromoester compound (1) (0·016 mol, 5·0 g), the hydroxyester compound (2) (0·014 mol, 4·0 g), and potassium carbonate (0·057 mol, 7·9 g) was refluxed for 16 hours in acetone. The reaction solution was filtered. The filtrate was concentrated, and then recrystallized from ethanol, to yield 3·7 g of the objective monomer (a).

Finally, monomer (a) (1·15 mmol, 600 mg) was reacted for 14 hours at 60°C in 4 ml of THF using 2·5 mg of AIBN as the polymerization initiator. The polymerization reaction product was purified by column chromatography to yield 490 mg of polymer FLCP a1 (see figure 1).

In order to investigate the dependence of the helical pitch on molecular weight we fractionated the polymer using gel permeation chromatography (GPC). The transition temperatures and molecular weights ($M_n$) of these fractionated polymers are listed in table 1. The transition temperatures were determined by using both differential scanning calorimetry (DSC) and polarized optical microscope.

The polymers FLCP a2–a7 were synthesized in order to investigate the effects of copolymerization on the helical pitch.

4-Hydroxybenzoic acid (0·29 mol, 40·0 g) and (S)-(−)-2-methylbutanol (0·35 mol, 30·9 g) were refluxed for 20 hours in 150 ml of toluene in the presence of 1 ml of conc. sulphuric acid. The reaction solution was concentrated, and then purified by column chromatography to yield 53·2 g of 2-methylbutyl 4-hydroxybenzoate (3).

To an aqueous solution of 4-hydroxybenzoic acid (0·055 mol, 7·6 g) and sodium hydroxide (0·065 mol, 2·6 g) in 200 ml of water, carbobenzoxychloride (0·065 mol, 10·6 g) was added dropwise at 0°C. After 24 hours, the precipitate was washed with

Table 1.    Molecular weight ($M_n$) and transition temperatures on cooling of FLCP a1.

| | | Transition temperature/K | | |
|---|---|---|---|---|
| FLCP | $M_n$ | g–$S_C^*$ | –$S_A$ | –I |
| a1 | $4{\cdot}0 \times 10^3$ | 295 | 303 | 363 |
| | $5{\cdot}0 \times 10^3$ | 299 | 304 | 369 |
| | $9{\cdot}0 \times 10^3$ | 301 | 307 | 378 |
| | $1{\cdot}5 \times 10^4$ | 302 | 308 | 383 |

$CH_2=CHCOO(CH_2)_{12}O-\langle O \rangle-COO-\langle O \rangle-COOCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$

$CH_2=CHCOO(CH_2)_{12}O-\langle O \rangle-COO-\langle O \rangle-OCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$

$-(CH_2CH)_{\overline{1-m}}-(CH_2CH)_{\overline{m}}-$

$\overset{|}{C}OO(CH_2)_{12}O-\langle O \rangle-COO-\langle O \rangle-OCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$

$\overset{|}{C}OO(CH_2)_{12}O-\langle O \rangle-COO-\langle O \rangle-COOCH_2\overset{CH_3}{\underset{*}{C}HC_2H_5}$
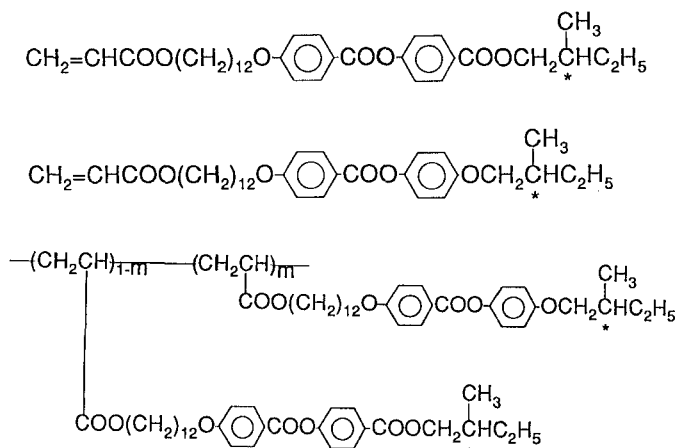
Figure 2. Molecular structures of the monomer (b), monomer (c), and the polymer FLCP a2–a7, where *m* represents the composition of copolymers.

water, filtered, dried, and then purified by column chromatography to yield 15·0 g of 4-benzyloxycarbonyloxybenzoic acid (4).

A solution of compound (4) (0·027 mol, 7·3 g) and phosphorus pentachloride (0·027 mol, 5·6 g) in 50 ml of ether was stirred for 24 hours at room temperature. The reaction mixture was deetherized and the obtained crystal was recrystallized from hexane, to yield 4·5 g of 4-benzyloxycarbonyloxybenzoyl chloride (5).

A solution of compound (3) (0·016 mol, 3·3 g) in 20 ml of THF and 40 ml of pyridine was cooled, and a solution of compound (5) (0·01 mol, 2·9 g) in THF was added dropwise. The mixture was brought slowly to room temperature, then stirred for 8 hours. The reaction mixture was ether extracted and concentrated, then purified by column chromatography to yield 2·9 g of 2-methylbutyl 4-(4'-benzyloxycarbonyloxybenzoyloxy)benzoate (6).

A solution of compound (6) (6·0 mmol, 2·8 g) and 0·5 g of palladium carbon (5 per cent catalyst) in ethyl acetate was reacted for 4 hours in an atmosphere of hydrogen gas. The palladium carbon was filtered out using a membrane filter, the filtrate was concentrated, and then purified by column chromatography, to yield 1·26 g of 2-methylbutyl 4-(4'-hydroxybenzoyloxy)benzoate (7).

An acetone solution of the bromoester compound (1) (3·9 mmol, 1·2 g), compound (7) (3·3 mmol, 1·1 g) and potassium carbonate (15 mmol, 2·1 g) was refluxed for 8 hours. The reaction solution was filtered and concentrated, then purified by column chromatography and recrystallized from ethanol to yield 0·99 g of the objective monomer (b).

*p*-Toluenesulphonyl chloride (0·11 mol, 21·0 g) was dissolved in toluene and added to a mixture of (S)-(−)-2-methylbutanol (0·1 mol, 8·8 g) and pyridine (0·11 mol, 8·7 g) also dissolved in toluene. The mixture was stirred for 24 hours at room temperature. After the reaction, the toluene was removed under reduced pressure. The residue was purified by column chromatography yielding 18·9 g of 2-methylbutyl toluenesulphonate (8).

Hydroquinone (0·16 mol, 17·6 g) and compound (8) (0·078 mol, 18·9 g) were dissolved in ethanol under a nitrogen atmosphere. Potassium hydroxide (0·16 mol, 9·0 g) was added. The solution was refluxed for 16 hours and acidified with dil. HCl. The

Table 2. Composition of copolymers (see figure 2) and transition temperatures on cooling of FLCPs, where $m = [m_c]/([m_b] + [m_c])$. ($[m_b]$ is the concentration of monomer (b), and $[m_c]$ the concentration of monomer (c).)

| FLCP | $m$ | Transition temperature/K | | |
|------|-----|--------|--------|-----|
| | | g–$S_C^*$ | –$S_A$ | –I |
| a2 | 0·0 | 278 | 304 | 368 |
| a3 | 0·2 | 282 | 310 | 367 |
| a4 | 0·4 | 301 | 313 | 370 |
| a5 | 0·6 | 310 | 321 | 369 |
| a6 | 0·8 | 315 | 325 | 370 |
| a7 | 1·0 | 315 | 326 | 369 |

inorganic compound was filtered off and the solvent removed by evaporation. The residue was purified by column chromatography to yield 7·5 g of 4-(2-methylbutyloxy)phenol (**9**).

To obtain monomer (c) we used the same method used to obtain monomer (b) by employing compound (**9**) instead of compound (**3**).

Finally, the polymers FLCP a2–a7 were obtained from a mixture of monomer (b) and monomer (c) by free radical polymerization (see figure 2). We defined $m$ as the ratio of the two monomers used for the free radical polymerization reaction, i.e. $m = [m_c]/[m_b] + [m_c]$ ($[m_b]$ is the concentration of monomer (b), and $[m_c]$ the concentration of monomer (c)).

The transition temperatures of the copolymers are listed in table 2. Each sample was laminated with two ITO-coated glass plates using PET films as a spacer. The thickness of the PET films was either 25 $\mu$m or 100 $\mu$m. The cell was mounted on a Mettler FP 82 hot stage, and the temperature was controlled by a Mettler FP 80 central processor.

At first the cell was heated above the $S_A$–I transition temperature, i.e. into the isotropic phase and then slowly cooled to the $S_A$ phase. The cooling rate was 0·3–1 K min$^{-1}$. In this way we obtained large, homogeneously aligned monodomains (about 100 $\mu$m in diameter).

In the $S_C^*$ phase we observed a typical fan-shaped texture with equidistant lines caused by helical structures. Figure 3 shows a typical texture of the $S_C^*$ phase observed in a 100 $\mu$m thick cell of FLCP a7 under a polarized optical microscope. The pitch values were determined by measuring the distance of the lines.

### 3. Results and discussion

Figure 4 shows the dependence of the helical pitch $p$ of FLCP a7 on the temperature $T$. At the temperature just below the $S_A$–$S_C^*$ transition temperature, $T_C$, the equidistant lines were not clear. The equidistant lines however could be observed clearly in the temperature range $T_C$–$T > 1$ K. Therefore we measured the helical pitch in this temperature range. In the temperature range $T_C$–$T > 5$ K, the pitch values scarcely changed.

Figure 5 shows the dependence of the helical pitch of FLCP a1 on the molecular weight ($M_n$). The pitch values were measured at $T_C$–$T = 5$ K. From the previous result, the pitch values become stable at this temperature. The pitch values increased with increasing molecular weight of the FLCPs. In the $S_C^*$ phase, the helical structure is
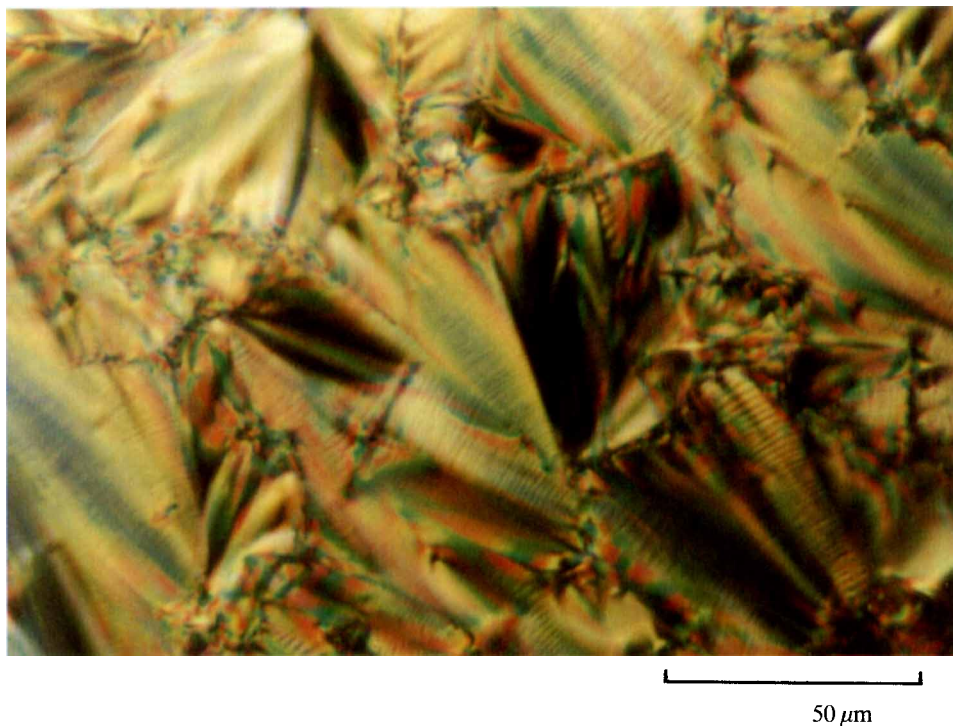
50 μm

Figure 3.   Photomicrograph of FLCP a7 in a 100 μm thick cell at 316 K.
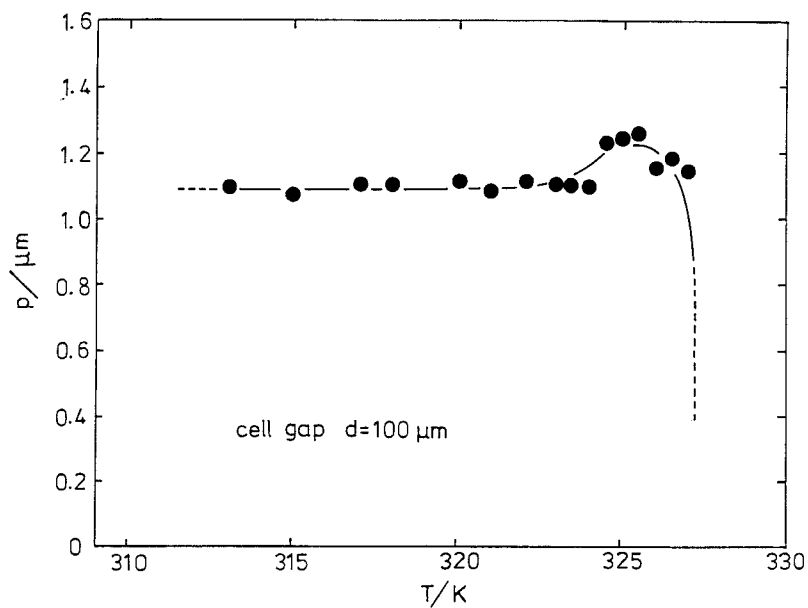


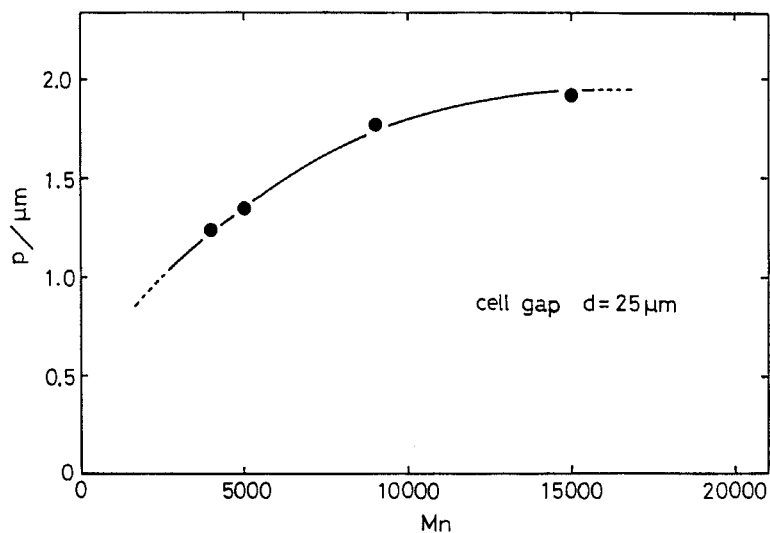Figure 4.   Temperature dependence of the helical pitch of FLCP a7 in a 100 μm thick cell.

Figure 5.    Dependence of the helical pitch of FLCP a1 on molecular weight ($M_n$). The pitch values were measured in a 25 μm thick cell at $T_C-T = 5$ K.
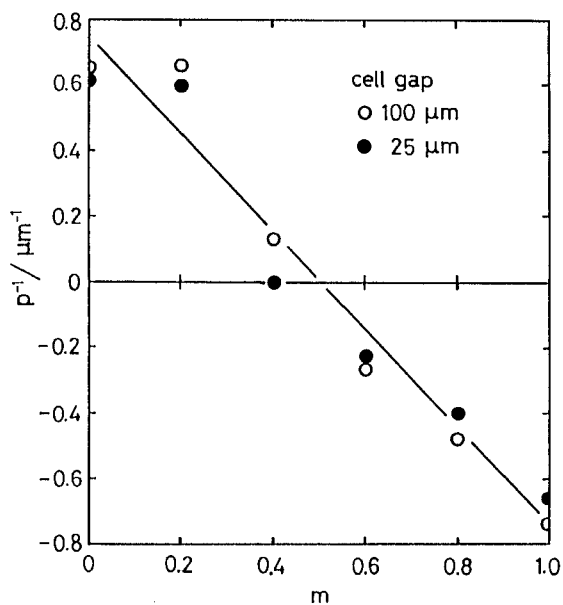


Figure 6.    Dependence of the helical pitch on composition of copolymers ($m$). The pitch values were measured at $T_C-T = 5$ K.

caused by interaction between chiral parts of neighbouring smectic layers [9]. Therefore the increase of helical pitch suggests a decrease in this interaction. From this result, when the molecular weight increases the interaction between neighbouring smectic layers is weakened.

Subsequently we measured the helical pitch of copolymers. These copolymers contain two kinds of side chain units, which have different chiral parts respectively. One contains a (S)-2-methylbutyl ester chiral, and the other contains a (S)-2-methylbutyl ether chiral. The former is supposed to generate a right-handed helical structure, the latter a left-handed helical structure.

The helical pitch in low molar mass ferroelectric liquid crystals increases on mixing right- and left-handed chiral components [7, 8]. We can also expect the helical pitch to increase in a copolymer system.

Figure 6 shows the change of a helical pitch $p$ against the composition of copolymers ($m$). In this figure, the sign of $p^{-1}$ represents the sense direction of helicoidal twist. A positive sign represents a right-handed sense and a negative sign a left-handed sense. It is obvious that the helical pitch expands in the copolymers. The $p^{-1}$ value almost exhibits a linear dependence on the composition of the copolymers ($m$). It seems that the helical pitch becomes infinity when the composition of copolymers is nearly 0·5. In all compositions, the pitch value of a 25 $\mu$m cell was larger than that of a 100 $\mu$m cell. This is caused by wall anchoring effects, which were reported by Kondo *et al.* [10].

In the case of FLCP a4 ($m=0\cdot4$) the pitch value was so large that the helical structures vanished in the 25 $\mu$m cell due to the wall anchoring effect, however the helical structures remained in the 100 $\mu$m cell.

## 4. Conclusion

The helical pitch of ferroelectric liquid-crystalline polymers and copolymers was measured. The pitch increases with increasing polymers molecular weight in homo-polymers and increased according to relative amounts of right- and left-handed chiral side chains in the copolymers.

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