Liquid Crystals

Effect of a lateral substituent on the mesomorphic properties of ferroelectric side chain liquid crystalline polysiloxanes

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Effect of a lateral substituent on the mesomorphic properties of ferroelectric side chain liquid crystalline polysiloxanes

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The synthesis of side chain liquid crystalline polysiloxanes containing oligooxyethylene spacers and (S)-2-methylbutyl 4-[(4-oxybiphenyl-4′-yl)carbonyloxy]-3-fluorobenzoate mesogenic side groups is presented. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction measurements reveal liquid crystalline properties for all synthesized monomers and polymers. All three precursor olefinic monomers reveal cholesteric and smectic A phases. The olefinic monomer which contains two oligooxyethylene units in the spacer is the only one which reveals a twist grain boundary A phase and a blue phase, besides the cholesteric and smectic A phases. All three polysiloxanes present enantiotropic smectic A and chiral smectic C phases. The mesomorphic behaviours of the monomers and polymers are compared with those of the corresponding monomers and polymers without the lateral fluoro substituent. The results seem to demonstrate that incorporating a lateral fluoro substituent in the mesogenic cores of the monomers affects not only the mesophase thermal stability, but also the nature of the mesophases formed. However, incorporating a lateral fluoro substituent in the mesogenic cores of the polymers affects only the thermal stability of the mesophases formed. The lateral fluoro substituent has a more profound effect on the mesomorphic behaviour for the monomers than that for the polymers.

1. Introduction

The potential application of ferroelectric liquid crystals (FLCs) in fast switching, high resolution electro-optical devices is well documented [1–3]. Besides low molar mass FLCs, a number of ferroelectric liquid crystalline side chain polymers have been successfully prepared during the past few years [4–27]. These polymers are interesting because of their ferroelectric properties and this field has been reviewed by LeBarney and Dubois [28]. However the detailed structure–property relationships of ferroelectric liquid crystalline polymers (LCPs) has not been clear until now. It seems necessary to introduce additional functional groups into the mesogenic units, spacers and polymer backbones of side chain liquid crystalline polymers to create some new property combinations in order to achieve these goals.

In our previous reports [29–31], the effects of polymer backbone and spacer on the formation and thermal stability of the chiral smectic C phase for ferroelectric side chain LCPs have been extensively studied. The results demonstrate that the tendency towards a chiral smectic C phase increases with increasing spacer length and flexibility of the polymer backbone, and the oligoox-

ethylene spacer can dramatically increase the thermal stability of the chiral smectic C phase.

Investigations of the effect of lateral substituents on liquid crystalline behaviour may have several objectives, such as the desire to determine to what extent clearing points and the relative stabilities of different mesophases are affected by the size and type of lateral substituents or to find out how physical properties, e.g. dielectric anisotropy, elastic constants and viscosity are modified. The effect of molecular structure on the occurrence of tilted smectic C phases is very different from that on nematic or orthogonal smectic phases. The molecules should possess some degree of steric asymmetry, so that they can arrange themselves in a tilted layer when packed together. The influence of a lateral substituent on the formation of a chiral smectic C phase for low molar mass liquid crystals has been studied by Coates et al. [32]. Their experimental results demonstrated that incorporation of a lateral substituent in the mesogenic core of a molecule reduces the occurrence of higher ordered smectic phases, and also decreases their melting point in most cases. According to some other reports on low molar mass liquid crystals in the literature [33, 34], introducing a suitable lateral substituent, e.g. fluoro, into the mesogenic cores can enhance the formation of a tilted smectic C phase.

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In this study, a series of new side chain liquid crystal-line polysiloxanes containing oligooxethylene spacers and the (S)-2-methylbutyl 4-[(4-oxybiphenyl-4′-yl)car-bonyloxy]-3-fluorobenzoate mesogenic side group have been synthesized. Their characterization by differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction is presented. The effect of a lateral fluoro substituent on the mesomorphic properties of the monomers and polymers obtained is discussed.

2.   Results and discussion

The synthetic route used for the preparation of monomers **IM–IIIM** is outlined in scheme 1. The chiral end group was inserted into these mesogenic compounds starting with commercially available (S)-(−)-2-methyl-butan-1-ol. This was done by a sequence of reactions which avoided racemization. Three monomers were characterized by differential scanning calorimetry and optical polarizing microscopy. The DSC thermograms of monomer **IM** are presented in figure 1. Monomer **IM**
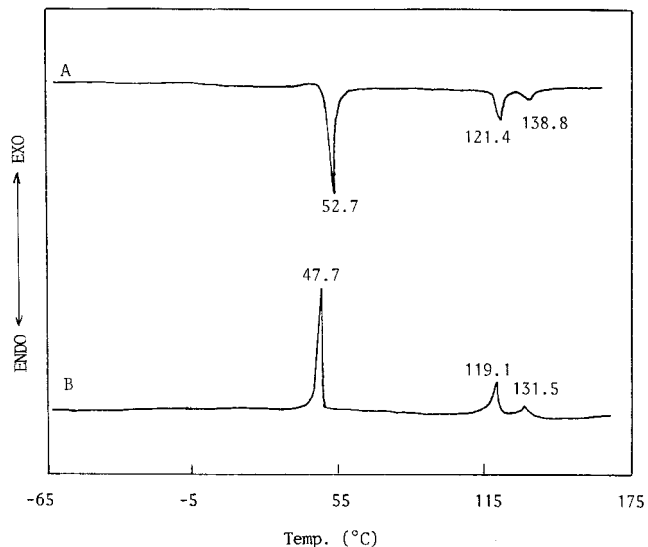
Figure 1.   DSC thermograms of monomer **IM** $(10°C\,min^{-1})$: (a) heating scan; (b) cooling scan.
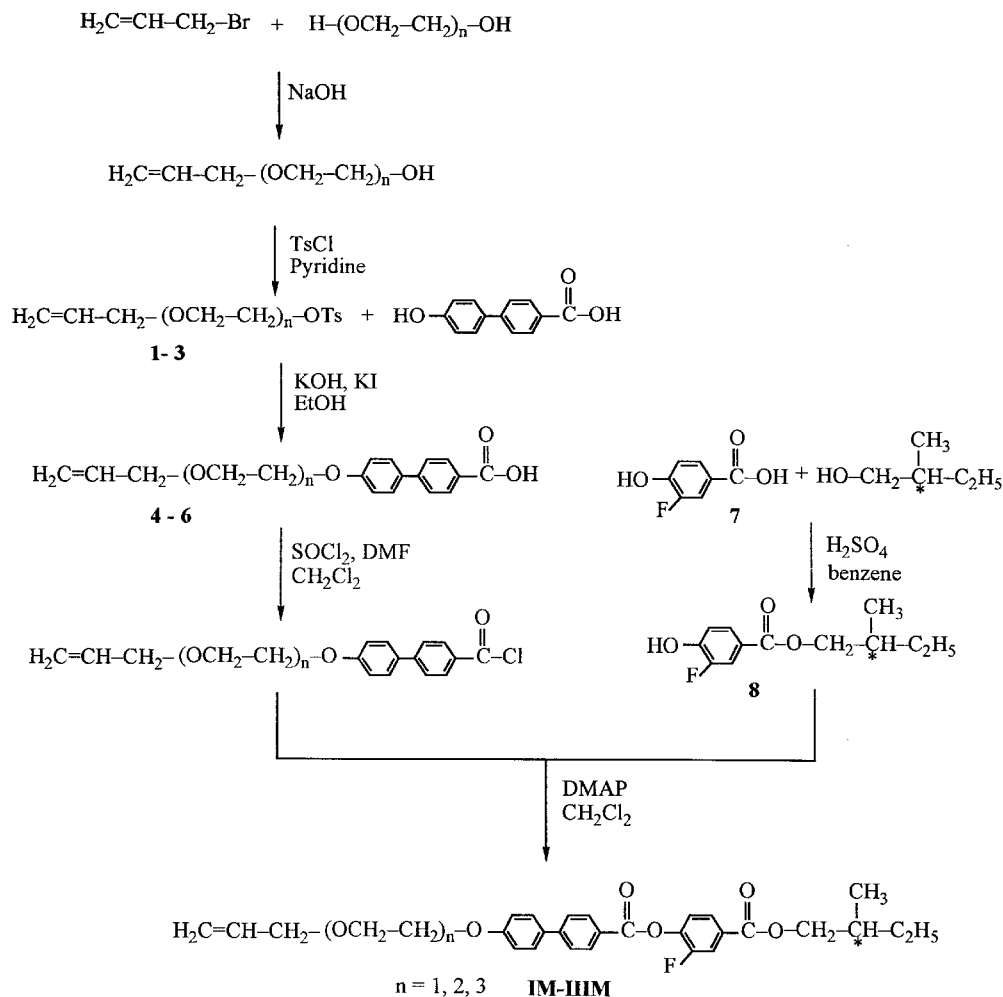
Scheme 1.   Synthesis of monomers **IM–IIIM**.

(a) (b)
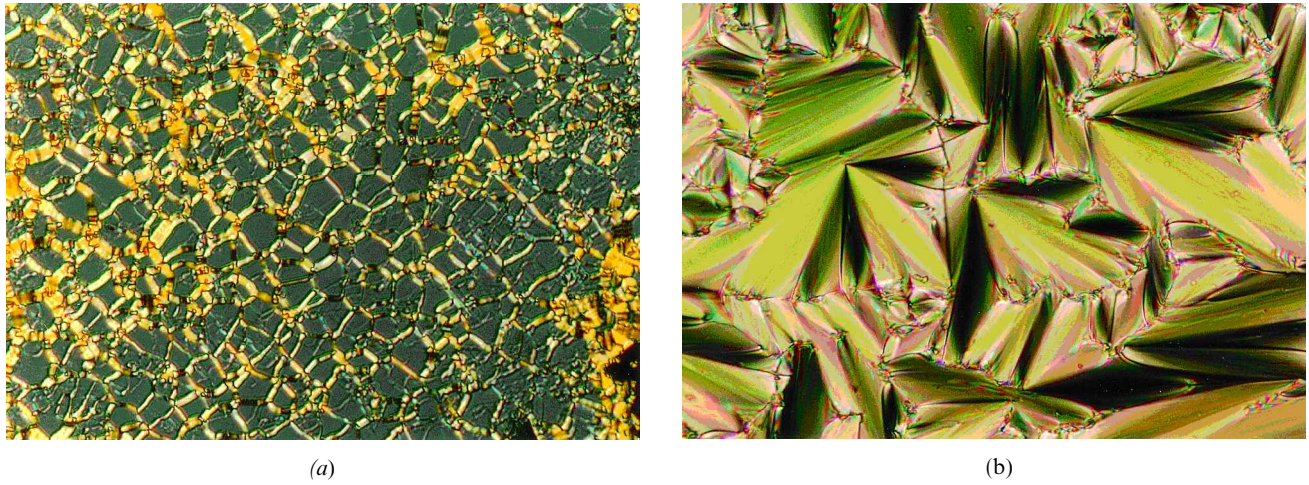
Figure 2.   Optical polarizing micrographs displayed by **IM**: (*a*) cholesteric texture obtained at 121·7°C; (*b*) smectic A texture obtained at 110·0°C.

(a) *(b)*

(c) *(d)*
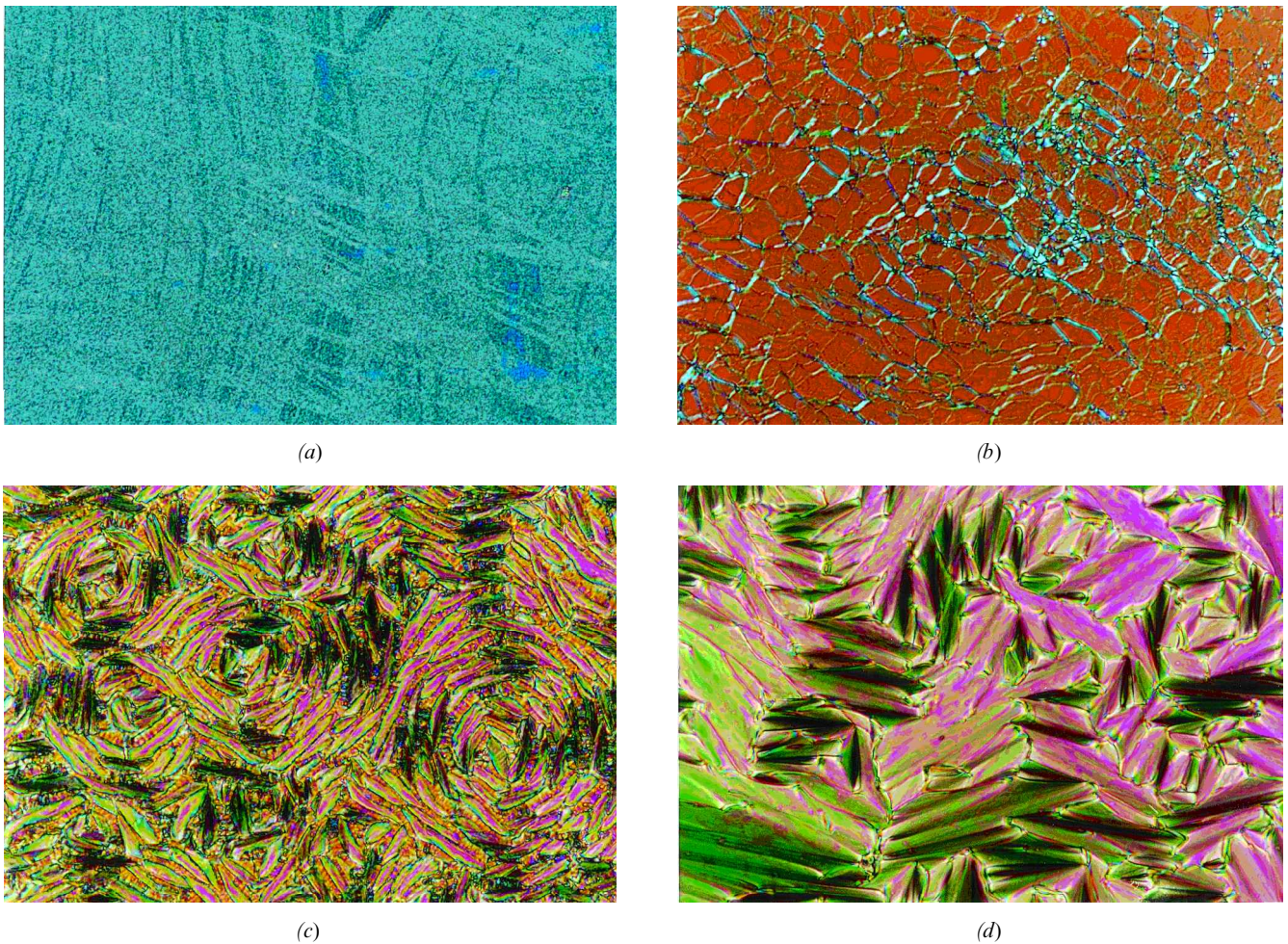
Figure 4.   Optical polarizing micrographs displayed by **IIM**: (*a*) blue phase obtained at 81·5°C; (*b*) cholesteric texture obtained at 80·0°C; (*c*) twist grain boundary A texture obtained at 72·8°C; (*d*) smectic A texture obtained at 70·0°C.

exhibits a melting transition at 52·7°C, a smectic A to cholesteric transition at 121·4°C, and a cholesteric to isotropic phase transition at 138·8°C on the heating scan (curve A). The cooling scan (curve B) looks almost identical to the heating scan, except that a very small supercooling (less than 5°C) is observed for the exothermic transitions. Figures 2(a) and 2(b) display the typical smectic A and cholesteric textures exhibited by **IM**.

Monomer **IIM** reveals a very unusual mesomorphic behaviour. Five thermal transitions are observed on both DSC heating and cooling scans (curves A and B in figure 3). Optical microscopic observation verified the formation of smectic A, twist grain boundary A, cholesteric and blue phases for monomer **IIM** (see figures 4(a) to (d)). The twist grain boundary A (*TGBA*) phase which is a new type of liquid crystalline phase, was discovered by Goodby *et al.* in 1989 [35,36]. This mesophase predicted by de Gennes [37] and Renn and Lubensky [38], is made up of smectic A blocks which rotate around a direction perpendicular to the molecular long axis and in the plane of the smectic layers. The smectic blocks are separated by a lattice of screw or edge dislocations. Therefore, the twist grain boundary A phase is also called the helical smectic A phase SmA*.

Monomer **IIIM**, containing three oxyethylene units in the spacer, exhibits only smectic A and cholesteric phases on both DSC heating and cooling scans. Table 1 summarizes the thermal transitions and phase transition enthalpies of monomers **IM–IIIM**. The thermal transitions and the thermodynamic parameters of monomers **IVM–VIM** which have been reported previously [29], are also reported in table 1 for comparison. As can be

seen from the data listed in table 1, monomers **IVM–VIM** without a lateral fluoro substituent, exhibit smectic A and chiral smectic C phases, while monomers **IM–IIIM** with a lateral fluoro substituent, reveal smectic A and cholesteric phases. Monomer **IIM** is the only one which presents the twist grain boundary A and blue phases besides the smectic A and cholesteric phases. The results seem to demonstrate that incorporating a lateral fluoro substituent in the mesogenic cores dramatically reduces not only the isotropization temperature of a monomer but also the tendency to give a chiral smectic C phase.

The synthesis of polymers **IP–IIIP** is described in scheme 2. Excess of olefinic monomers was usually used to carry the hydrosilylation reaction to completion. The unreacted monomers were removed by several reprecipitations from THF solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity. The polymers were characterized by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction. Figure 5 presents representative DSC thermograms of polymer **IP**. Polymer **IP** shows a glass transition at 0·9°C followed by a chiral smectic C to smectic A phase transition at 153·4°C and a smectic A to isotropic phase transition at 168·5°C. The cooling scan looks almost identical to the heating scan, except that a very small supercooling (less than 5°C) is observed for both exothermic transitions. Both polymers **IIP** and **IIIP** present very similar DSC thermograms to those of polymer **IP**. On the heating scan, polymer **IIP** gives a glass transition at −8·0°C, followed by a chiral smectic C to smectic A phase transition at 157·9°C and a smectic A to isotropic phase transition at 160°C, while polymer **IIIP** gives a glass transition at −12·5°C, followed by a chiral smectic C to smectic A phase transition at 142·1°C and a smectic A to isotropic phase transition at 148·0°C. Parts (a) and (b) of figure 6 show representative smectic A and chiral smectic C textures for polymer **IP**. The phase assignment was also checked by X-ray diffraction.

Figure 7 shows the temperature-dependent *d*-spacing of the smectic layers obtained from powder samples of **IP**. The *d*-spacings of the smectic layers are 30·49 Å at 154°C, 29·20 Å at 140°C, 28·56 Å at 90°C and 28·12 Å at 30°C. When the measuring temperature falls from 154 to 140°C, the *d*-spacing given by the first-order reflection gradually decreases from 30·49 to 29·20 Å. This gives strong evidence for the formation of the tilted chiral smectic C phase. This result is also in agreement with the formation of a chiral smectic C phase since the tilt angle of the side chains is known to increase gradually with decreasing temperature for chiral smectic C side chain LCPs. Temperature-dependent X-ray diffraction results for polymers **IIP** and **IIIP** are also shown in
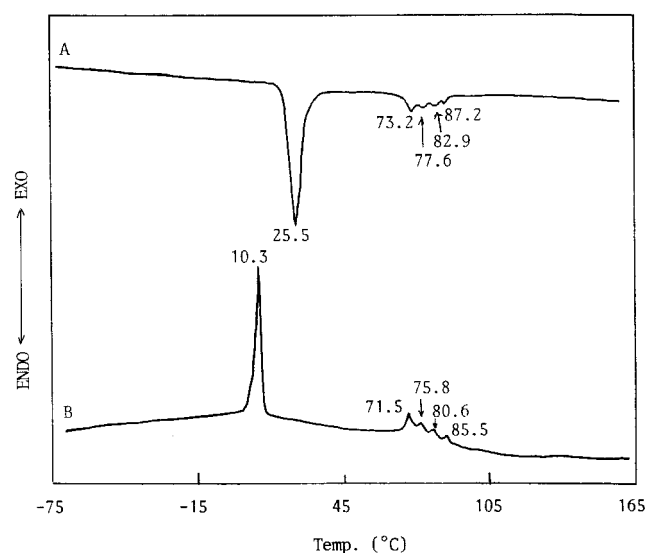

Figure 3.   DSC thermograms of **IIM** (10°C min⁻¹): (a) heating scan; (b) cooling scan.

Table 1. Phase transitions and phase transition enthalpy changes for monomers **IM–IVM**.

Monomer	n	Phase transitions/°C (Corresponding enthalpy changes/kcal mol^{-1})[a] heating cooling
IM	1	Cr 52·7(1·35)SmA 121·4(0·33)N* 138·8(0·06)I I 131·5(0·08)N* 119·1(0·3)SmA 47·7(1·06)Cr
IIM	2	Cr 25·5(3·15)SmA 73·2(0·26)TGBA 77·6(0·2)N* 82·9(0·13)BP 87·2(0·02)I I 85·5(0·07)BP 80·6(0·13)N* 75·8(0·17)TGBA 71·5(0·2)SmA 10·3(1·36)Cr
IIIM	3	Cr 16·6(3·02)SmA 44·7(0·03)N* 51·1(0·14)I I 49·6(0·08)N* 42·8(0·26)SmA − 10·5(0·84)Cr
IVM[b]	1	Cr 95·4(5·36)SmA 171·5(1·16)I I 168·8(1·16)SmA 76·8(—)SmC* 58·1(1·48)Cr
VM[b]	2	Cr 20·5(0·99)SmC* 72·5(0·03)SmA 140·2(0·82)I I 138·5(0·76)SmA 69·1(0·03)SmC* 12·1(0·98)Cr
VIM[b]	3	Cr 7·6(0·93)SmC* 57·4SmA 106·6(0·73)I I 103·2(0·75)SmA 54·5(0·01)SmC* 1·4(0·80)Cr

[a] Cr=crystalline, SmA=smectic A, TGBA=twisted grain boundary A, SmC*=chiral smectic C, N*=cholesteric, BP=blue phase, I=isotropic.
[b] Data obtained from ref. [30].
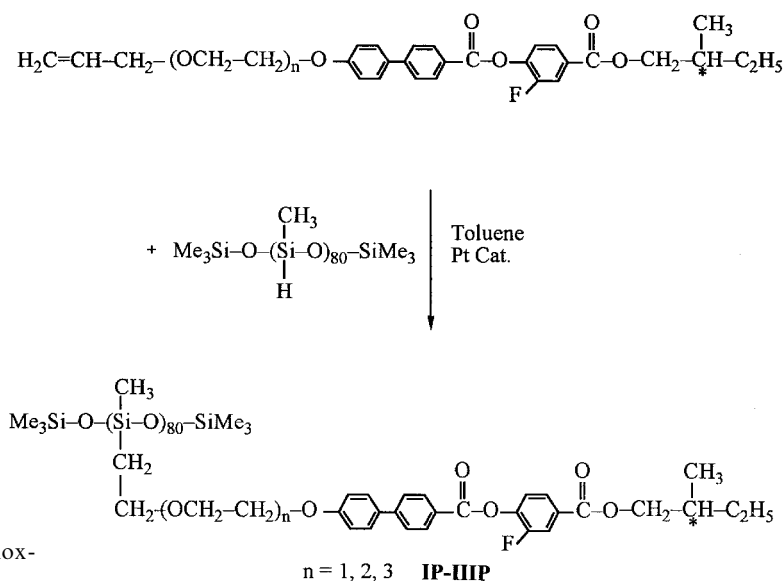
Scheme 2. Synthesis of polysiloxanes **IP–IIIP**.

figure 7. Both polymers also reveal smectic A and chiral smectic C phases. The *d*-spacings of the smectic layers of polymer **IIP** are 33·86 Å at 150°C, 32·95 Å at 135°C, 32·24 Å at 85°C and 31·76 Å at 30°C, while those for polymer **IIIP** are 36·51 Å at 148°C, 35·30 Å at 130°C, 34·81 Å at 80°C and 34·63 Å at 35°C. The ferroelectric properties of polymers **IP–IIIP** have also been studied by broad band dielectric relaxation and are reported elsewhere [39].

Table 2 summarizes the thermal transitions and corresponding enthalpy changes for polymers **IP–IIIP** which contain a lateral fluoro substituent in the meso-

genic moieties. All three polymers form enantiotropic smectic A and chiral smectic C phases, although their corresponding monomers give cholesteric and smectic A phases. It is well-documented in many cases that the mesophase formed by a side chain LCP is more organized than that exhibited by the corresponding monomer; this is the so-called 'polymer effect' for side chain LCPs. In order to study the lateral substituent effect on the mesomorphic behaviour of the new polymers, table 2 also lists the thermal transitions and the corresponding enthalpy changes for polymers **IVP–VIP** which contain no fluoro substituent in the mesogenic side chains [30].
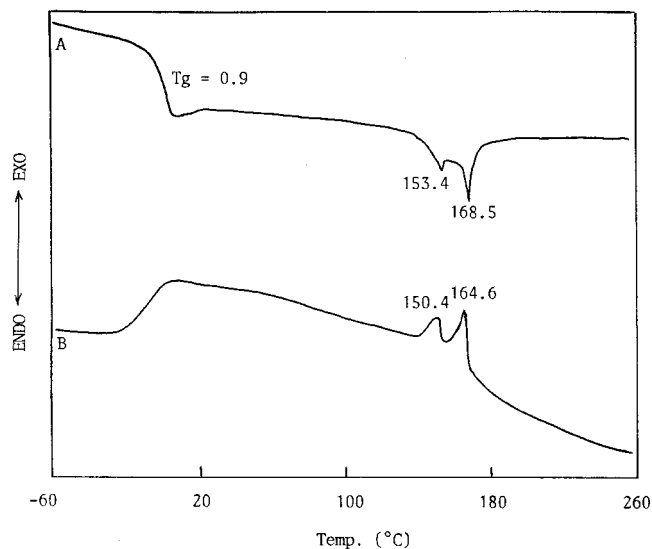
Figure 5. DSC thermograms of polymer **IP** ($10°C \, min^{-1}$): (*a*) heating scan; (*b*) cooling scan.

As can be seen from the data listed in table 2, all six polymers exhibit enantiotropic smectic A and chiral smectic C phases.

The experimental results indicate that incorporating a lateral fluoro substituent into the mesogenic core of a side chain LCP does not change the nature of the mesophases formed, but decreases the thermal stability of the mesophases including that of the chiral smectic C phase. Nevertheless, polymers **IP–IIIP** still produce very wide temperature ranges (about 150 to 160°C) of chiral smectic C phase. These results again indicate that the nature of the flexible oligooxyethylene spacer plays a very important role with respect to the thermal stability of the chiral smectic C phase.

Spontaneous polarizations of both series of polymers were also evaluated. A voltage of 6 V was applied to a $5 \, \mu m$ thick cell. Figure 8 presents the polarization (P_s) as a function of temperature for polymers **IIP** and **VP**. The P_s values of polymers **IIP** and **VP** are 21·4 and $12·4 \, nC \, cm^{-2}$ at 60°C. This experimental result demonstrates that incorporating a lateral fluoro substituent into the mesogenic core of this LCP decreases its P_s value.

3. Experimental
3.1. *Materials*

Poly(methylhydrogensiloxane) ($\overline{Mn} = 2270$) and divinyltetramethyldisiloxane platinum catalyst were obtained from Petrarch system Inc. and were used as received. (*S*)-(−)-2-Methylbutan-1-ol, $[\alpha]_D^{25} = -6·5°$ (from Merck Ltd), 2-allyloxyethanol and 4-hydroxy-biphenyl-4′-carboxylic acid (from Tokyo Kaisei Co.) and all other reagents (from Aldrich) were used as received. Toluene used in the hydrosilylation reaction was first
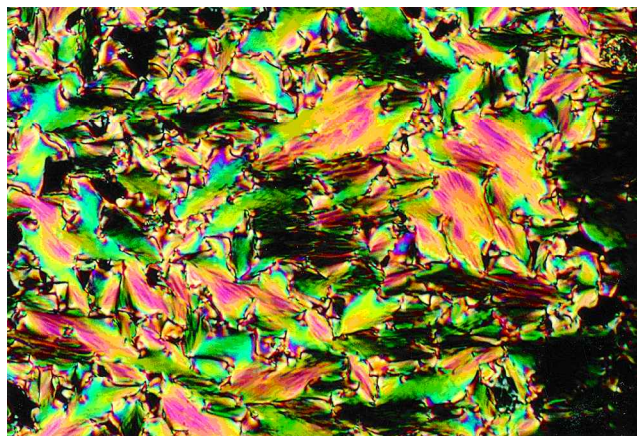
(*a*)
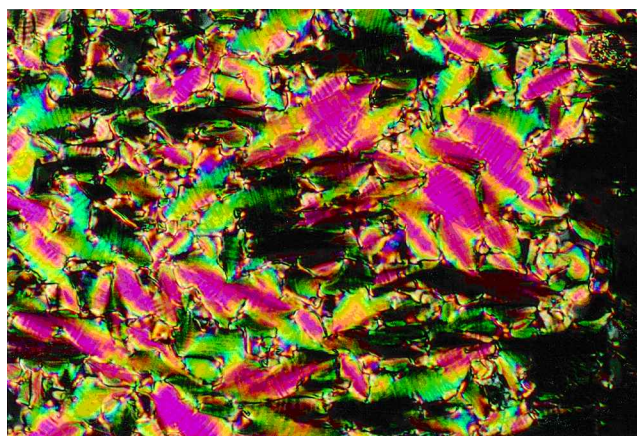
(*b*)

Figure 6. Optical polarizing micrographs displayed by polymer **IP**: (*a*) smectic A texture obtained at 155·0°C; (*b*) chiral smectic C texture obtained at 140·0°C.

heated under reflux over sodium and then distilled under nitrogen.

3.2. *Techniques*

^{1}H NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FTIR spectra were measured using a Nicolet 520 FTIR spectrometer. Polymer samples were cast as films on a KBr tablet for the IR measurements. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were $10°C \, min^{-1}$. Thermal transitions reported were collected during the second heating and cooling scans. A Carl Ziess Axiophot optical polarizing microscope equipped with a Mettler FP82 hot stage and an FP80 central processor was used to observe the thermal transitions and to analyse the anisotropic textures. Preparative gel permeation chromatography (GPC) was carried out using a Waters 510 LC instrument equipped
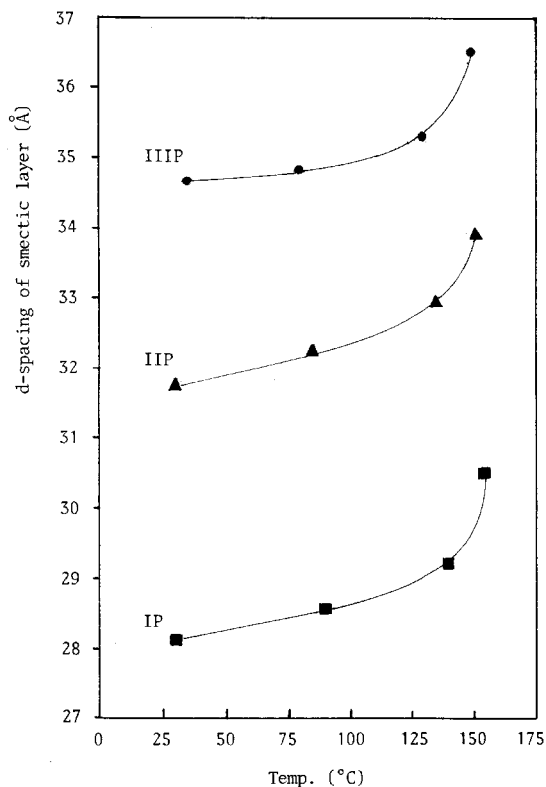
Figure 7. Temperature dependence of the smectic C layer spacings for polymers **IP** (■), **IIP** (▲) and **IIIP** (●).

Table 2. Phase transitions and phase transition enthalpy changes for polymers **IP–IVP**.

Polymer	n	Phase transitions/°C (Corresponding enthalpy changes/kcal mru^{-1})[a] heating cooling
IP	1	g 0·9SmC* 153·4(—)[b]SmA 168·5(0·66)I I 164·6(0·57)SmA 150·4(—)[b]SmC*
IIP	2	g−8·0SmC* 157·9(—)[b]SmA 160·0(0·87)I I 157·3(0·71)SmA 155·3(—)[b]SmC*
IIIP	3	g−12·5SmC* 142·1(—)[b]SmA 148·0(0·87)I I 144·8(0·77)SmA 139·8(—)[b]SmC*
IVP[c]	1	g 9·8SmC* 215·2(0·07)SmA 234·6(0·80)I I 229·2(0·73)SmA 211·7(0·03)SmC*
VP[c]	2	g−11·2SmC* 208·0(—)[b]SmA 211·8(0·85)I I 212·0(0·49)SmA 206(—)[b]SmC*
VIP[c]	3	g−25·1SmC* 168·0(—)[b]SmA 190·3(0·94)I I 184·2(0·98)SmA 161(—)[b]SmC*

[a] mru = mol repeating unit: g = glassy, S = smectic, SmA = smectic A, SmC* = chiral smectic C, I = isotropic.
[b] Overlapped transition.
[c] Data obtained from ref. [30].

with a 410 differential refractometer and a preparative GPC column (22·5 mm × 60 cm) supplied by American Polymer Standard Co. X-ray diffraction measurements were made with nickel-filtered CuK$_\alpha$-radiation with a Rigaku powder diffractometer. Optical rotations were measured at 25°C using a Jasco DIP-140 polarimeter with chloroform as solvent for all compounds. Spontaneous polarization was evaluated using a Displaytech (Boulder, Colorado, USA) APTIII automated property tester.

3.3. Synthesis of monomers

The synthesis of the olefinic monomers **IM–IIIM** used for hydrosilylation is outlined in scheme 1. 2-(2-Allyloxyethoxy)ethanol and 2-[2-(2-allyloxyethoxy)ethoxy]ethanol were synthesized according to a literature procedure [40].

The detailed synthetic procedures for compounds **1–6** in scheme 1 were reported in a previous publication [30].

3.3.1. 3-Fluoro-4-hydroxybenzoic acid (7)

3-Fluoro-4-hydroxybenzoic acid was prepared following a method reported in the literature [41].

3.3.2. (S)-2-Methylbutyl 3-fluoro-4-hydroxybenzoate (8)

3-Fluoro-4-hydroxybenzoic acid (3·0 g, 19·2 mmol), (S)-2-methylbutan-1-ol (2·61 g, 29·6 mmol), and concentrated sulphuric acid (0·2 ml) were added to 15 ml of dried benzene. The reaction mixture was heated under reflux until the 3-fluoro-4-hydroxybenzoic acid was completely dissolved and 0·35 ml of water had collected in a Dean–Stark trap. After cooling to room temperature, the solution was washed with 2% aqueous NaHCO$_3$ and water, and dried over anhydrous MgSO$_4$. The solvent was then removed by rotary evaporation and the solid purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1:1 as eluent) to yield 3·4 g (78%) of pale yellow crystals. $[\alpha]_D^{25}=+5\cdot6$ ($c=0\cdot32$ g cm^{-3} in chloroform). ^{1}H NMR (CDCl$_3$, TMS, ppm): $\delta 0\cdot90$–0·99 (m, 6H, –CH$_3$), 1·18–1·59 (m, 2H, –CH$_2$–), 1·75–1·89 (m, 1H, –CH(CH$_3$)–), 4·11 (ABd, 2H, –COOCH$_2$–), 6·95 (t, 1H, –O–ArH$_3$(F)–), 7·79 (d, 2H, –ArH$_3$(F)–COO–). C$_{12}$H$_{15}$O$_3$F: calcd: C 63·71, H 6·68; found: C 63·83, H 6·71 per cent.

3.3.3. (S)-2-Methylbutyl 4-[[4-(2-allyloxyethoxy)-biphenyl-4'-yl]carbonyloxy]-3-fluorobenzoate (IM), (S)-2-Methylbutyl 4-[[4-[2-(2-allyloxyethoxy)ethoxy]biphenyl-4'-yl]carbonyloxy]-3-fluorobenzoate (IIM), and (S)-2-Methylbutyl 4-[[4-[2-[2-(2-allyloxyethoxy)ethoxy]ethoxy]biphenyl-4'-yl]carboxyloxy]-3-fluorobenzoate (IIIM)

The olefinic monomers **IM–IIIM** were prepared by esterification using (S)-2-methylbutyl 3-fluoro-4-hyd-
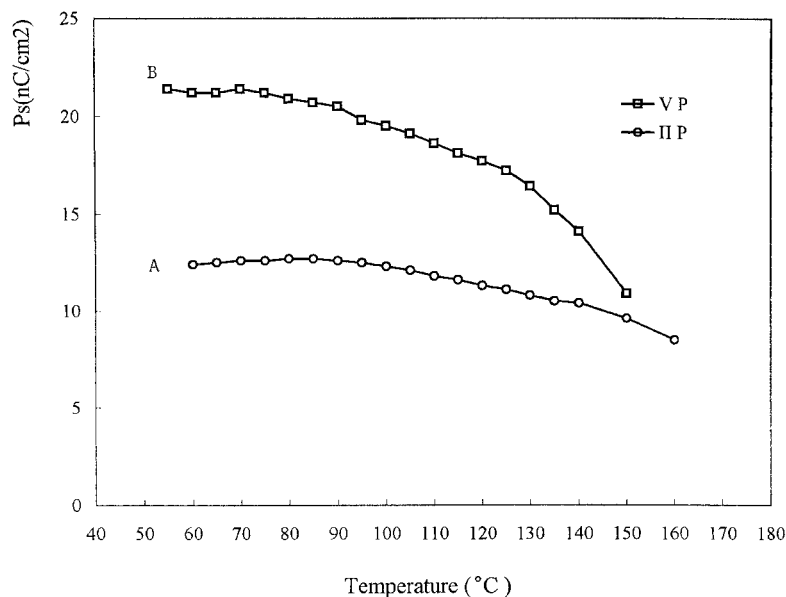
Figure 8.   Spontaneous polariza-
tion P_s versus temperature for
polymer **IIP** (○) and **VP** (■).

roxybenzoate and the corresponding acids **4–6**. The
synthesis of monomer **IIM** is described below.

4-[2-(2-Allyloxyethoxy)ethoxy]biphenyl-4′-carboxylic
acid (2·0 g, 5·8 mmol) was reacted at room temperature
with an excess of thionyl chloride containing a drop of
dimethylformamide in 7 ml of methylene chloride for
2 h. The solvent was removed under reduced pressure to
give the crude acid chloride. The product was dissolved
in 10 ml of methylene chloride and added slowly to
a   cold   solution   of   (S)-2-methylbutyl   3-fluoro-
4-hydroxybenzoate (1·56 g, 7·0 mmol) and 4-dime-
thylaminopyridine (0·85 g, 7·0 mmol) in 100 ml of methyl-
ene chloride. The solution was allowed to stir for 2 h
and then the solvent was removed by rotary evaporation.
The crude product was purified by column chromato-
graphy (silica gel, ethyl acetate/n-hexane = 1 : 3 as eluent)
to yield 1·32 g (43%) of white crystals. $[\alpha]_D^{25} = +5·86$
($c = 0·35$ g cm^{-3} in   chloroform). ^{1}H   NMR(CDCl$_3$,
TMS, ppm) δ 0·94–1·01 (m, 6H, –C$\underline{H}_3$), 1·11–1·59 (m,
2H, –CH(CH$_3$)–C$\underline{H}_2$–), 1·81–1·95 (ABd, 1H, –C$\underline{H}$
(CH$_3$)–), 3·59 (d, 2H, †CH–C$\underline{H}_2$–) 4·11–4·24 (m, 10H,
–(OC$\underline{H}_2$C$\underline{H}_2$)$_2$– and –O–C$\underline{H}_2$–), 5·14 and 5·32 (2d, 2H,
$\underline{H}_2$C=d) 5·81–5·99 (m, 1H, =dC$\underline{H}$–), 6·96 (d, 2H,
biphenyl protons), 7·37 (t, 1H, –OAr$\underline{H}_3$(F)–), 7·60 (d,
2H, biphenyl protons), 7·71 (d, 2H, –Ar$\underline{H}_3$(F)–COO–],
7·91(d, 2H, biphenyl protons), 8·26 (d, 2H, biphenyl
protons). C$_{32}$H$_{35}$O$_7$F: calcd: C 69·80, H 6·41; found: C
69·83, H 6·50 per cent.

3.4.   *Synthesis of polysiloxanes* **IP–IIIP**

The synthesis of liquid crystalline polysiloxanes **1P–3P**
is outlined in scheme 2. A general synthetic procedure is
described below.

The olefinic derivative 1·0 g (10 mol % excess with

respect to the Si–H groups present in polysiloxane) was
dissolved in 100 ml of dry, freshly distilled toluene
together with the proper amount of poly(methylhydrog-
ensiloxane). The reaction mixture was heated to 110°C
under nitrogen and 100 µg of divinyltetramethyldisilox-
ane platinum catalyst was then injected with a syringe
as a solution in toluene (1 mg ml^{-1}). The reaction mix-
ture was heated under reflux (110°C) under nitrogen for
24 h. After this reaction time, FTIR analysis showed that
the hydrosilylation reaction was complete. The polymers
were separated, purified by several reprecipitations from
tetrahydrofuran solution into methanol, further purified
by preparative GPC, and then dried under vacuum.

4.   Conclusions

A series of new ferroelectric side chain liquid crystal-
line polysiloxanes containing oligooxyethylene spacers
and   4(S)-2-methylbutyl   [(4-oxybiphenyl-4′-yl)car-
bonyloxy]-3-fluorobenzoate side groups has been pre-
pared. All the polymers exhibit enantiotropic smectic A
and chiral smectic C phases. The synthesized polymers
IP–IIIP represent a system that contains a lateral fluoro
substituent. If they are compared with the corresponding
polymers **IVP–VIP** which contain no lateral fluoro
substituent, the former display the same mesomorphic
behaviour as the latter. However, the mesomorphic
temperature ranges exhibited by the former are much
narrower than those displayed by the latter. The experi-
mental results indicate that incorporating a lateral fluoro
substituent into the mesogenic core of a polymer can
decrease the thermal stabilities of the mesophases,
including the chiral smectic C phase.

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