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Side-chain liquid crystalline polysiloxanes containing a cyanohydrin chiral centre

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A number of new ferroelectric side chain liquid crystal homopolymers derived from poly(hydromethylsiloxane), their copolymers with different mesogens and with poly(dimethylsiloxane) backbones have been prepared. The transition temperatures of the monomers, homo and copolymers have been determined. The homopolymers exhibit S_C^* and N* phases, while copolymers show only a S_C^* phase. A measured spontaneous polarization value of monomer, 9b, is larger than $500\,nC\,cm^{-2}$.

1. Introduction

With increasing interest in ferroelectric liquid crystal displays (FLCDs), there has been considerable activity aimed at synthesizing new liquid crystalline materials with a large spontaneous polarization (P_s) and short response time. The spontaneous polarization of ferroelectric liquid crystals (FLCs) is connected with the chiral structure of the molecules. It was proposed in 1979 that ferroelectric properties are exhibited by certain low symmetry, smectic liquid crystals [1]. The S_C^* phase is the most fluid phase to offer such ferroelectric properties and/or has the greatest potential for electrooptic device applications. The development of the surface-stabilized ferroelectric liquid crystal (SSFLC) technique extends the potential of liquid crystal display systems by virtue of speed and bistability [2].

Liquid crystalline polysiloxanes are known to display low viscosity and low glass transition temperatures. Typically, the observed response times of ferroelectric liquid crystal polymers (FLCPs) have been in the millisecond range [3, 4]. Moreover FLCP systems, that combine the mechanical properties of polymeric materials and structural features of liquid crystals, have the possibility of helix unwinding to obtain a monodomain and obtain a high P_s value. To achieve high P_s FLC materials we have incorporated a strong dipolar group (CN) at the chiral centre [5]. The chiral centre is

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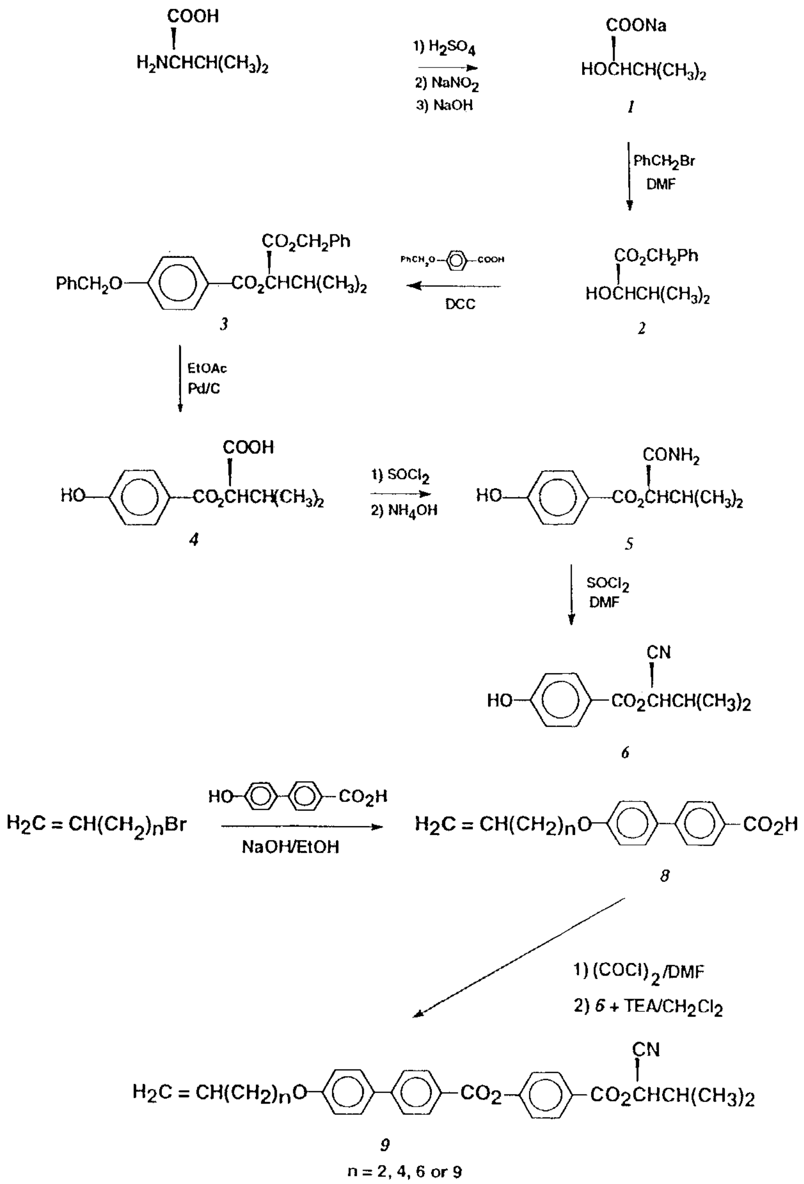
also coupled directly to the molecular core. This paper describes the synthesis and properties of four different types of polysiloxanes related to the following formulae.

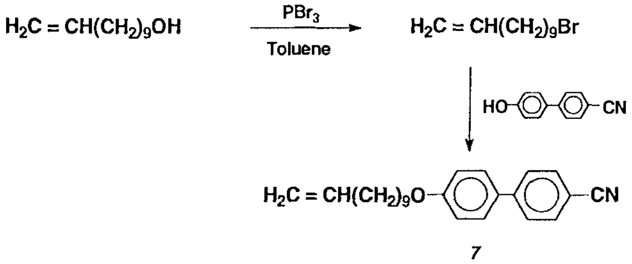
The synthesis of the vinyl moieties is shown in schemes 1 and 2. The polymers were prepared by the platinum catalysed hydrosilation of these vinyl moieties with poly(hydromethylsiloxane) (see scheme 3).

2. Experimental

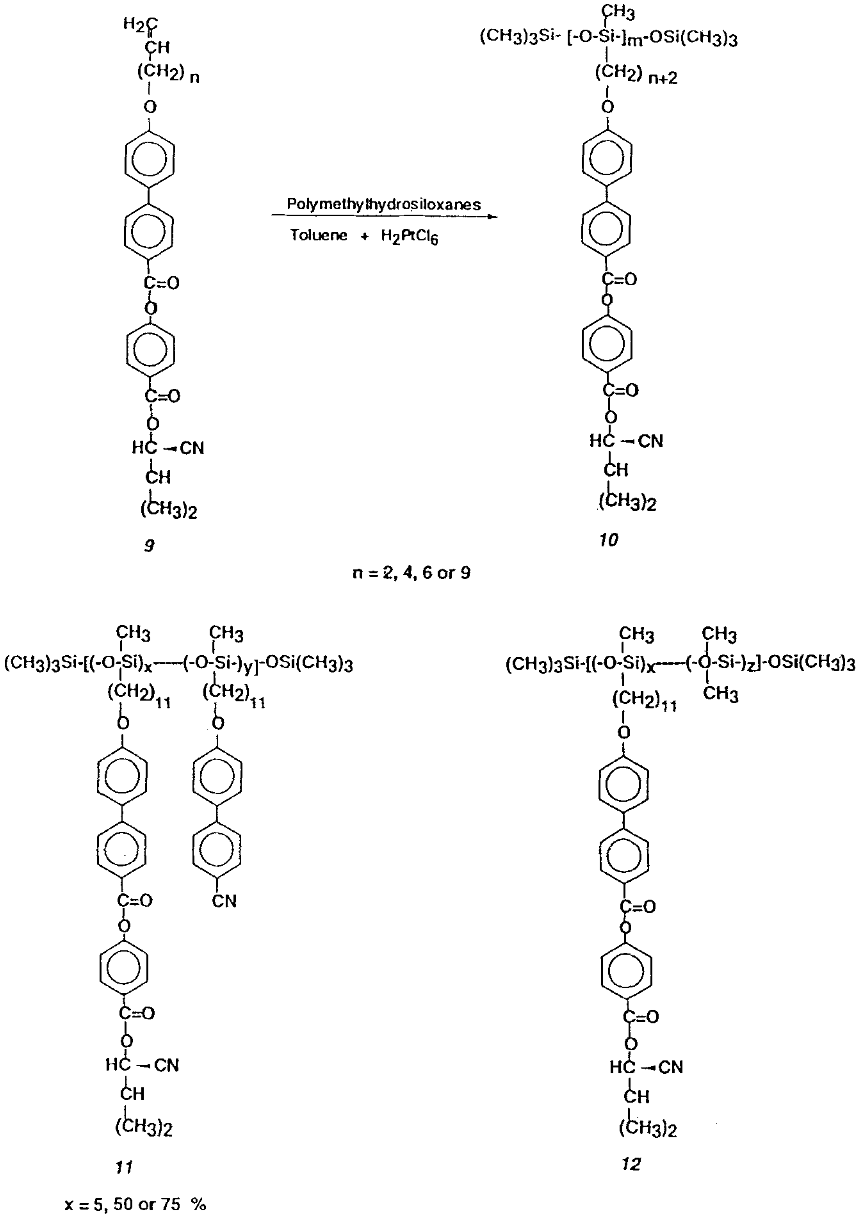
The infrared spectra were run on a Pye-Unicam 3-200 instrument and NMR spectra using a Varian 200 MHz Spectrometer. Specific rotations of the optically active compounds were determined using a Jasco DIP-360 digital polarimeter. Transition



Scheme 1.



Scheme 2.



Scheme 3.

temperatures for the intermediates and monomers were determined using a Leitz-Laborlux S polarizing microscope fitted with a Mettler FP-5 heating stage, and for polymers and copolymers using a Perkin-Elmer DSC-2 and DSC-7 spectrometer. The degrees of polymerization for the polymers and copolymers were determined using a Waters-510 HPLC with a Waters-410 differential refractometer.

2.1. *(S)-1-(Benzyloxycarbonyl)-2-methylpropyl 4'-benzyloxbenzoate* 3

Dicyclohexylcarbodiimide (DCC) (23·9 g, 0·116 mol) was added to a stirred mixture of 4-benzyloxybenzoic acid (24·1 g, 0·106 mol), (*S*)-benzyl 2-hydroxy-3-methylbutanoate (2) (22·0 g, 0·106 mol) and dimethylaminopyridine (DMAP) (1·3 g, 10·58 mmol) in sieve-dried dichloromethane (300 ml). The reaction mixture was stirred overnight at room temperature. The *N*, *N'*-dicyclohexylurea was filtered off and the filtrate washed with 5 per cent hydrochloric acid, water, dried ($MgSO_4$) and then filtered. The solvent was removed from the filtrate and the crude product purified by column chromatography on silica gel (60–100 mesh). Elution with ethyl acetate–hexane (10 per cent) gave a viscous product. Yield: 32·5 g (73·5 per cent); $[\alpha]_D^{25} = +0{\cdot}79°$ ($CHCl_3$). The product gave one spot from TLC and was used without further purification.

IR (film): 1750, 1710 cm^{-1}. NMR($CDCl_3$): δ 1·03 (d, 6H, $2CH_3$), 2·25–2·45 (m, 1 H, $\underline{H}$C–CH_3), 5·10 (d, 2 H, OCH_2Ph), 5·18 (d, 2 H, CO_2CH_2Ph), 6·84 (d, 2 H, Ar), 7·28–7·42 (m, 10 H, 2 Ph), 8·04 (d, 2 H, Ar).

2.2. *(S)-1-Carboxy-2-methylpropyl 4'-hydroxybenzoate* 4

A solution of compound (3) (3·20 g, 76·6 mmol) in ethyl acetate (150 ml) containing 10 per cent Pd/C (1·0 g) was hydrogenated at 50 psi at room temperature overnight. The catalyst was removed by filtration through Celite and the filtrate rotovaped to give a waxy material 4. Yield: 18·2 g (quantitative); $[\alpha]_D^{25} = +22{\cdot}89°$ ($CHCl_3$). NMR($CDCl_3$/DMSO): δ 1·00–1·20 (m, 6 H, 2 CH_3), 2·30–2·50 (m, 1 H, C$\underline{H}$–CH_3), 5·02 (d, 1 H, CO_2CH), 6·87 (d, 2 H, Ar), 7·94 (d, 2 H, Ar).

2.3. *(S)-1-Cyano-2-methylpropyl 4'-hydroxybenzoate* 6

The hydroxyacid (4) (18·0 g, 75·6 mmol) was initially converted into the acid chloride by reacting with oxalyl chloride (19·8 g, 0·151 mol) and sieve-dried dimethylformamide (2 drops) in sieve-dried benzene (100 ml) for 3 h at room temperature. The excess oxalyl chloride and the solvent were removed at 50–60°C under reduced pressure. The crude acid chloride residue was dissolved in diglyme (20 ml) and added to a stirred aqueous solution of ammonia (200 ml). The reaction mixture was stirred for 30 min at room temperature, then the amide (5) was filtered off, washed with water and dried *in vacuo*. Yield: 11·0 g (61·7 per cent).

A solution of thionyl chloride (33·7 ml, 0·46 mol) and sieve-dried dimethylformamide (100 ml) was added dropwise (30 min) to a vigorously stirred solution of the above amide (10·9 g, 46·6 mmol) in sieve-dried dimethylformamide (100 ml). The reaction mixture was stirred at room temperature for 10 h, then poured on to ice and the crude product extracted into ether. The combined ether extracts were washed with a saturated solution of sodium bicarbonate, water, dried ($MgSO_4$) and then filtered. After removal of the solvent, the product was purified by column chromatography on silica gel (60–100 mesh). Elution with dichloromethane gave 9·5 g (94·0 per cent) of the desired compound 6 as a viscous liquid; $[\alpha]_D^{25} = -29{\cdot}95°$ ($CHCl_3$). The product gave one spot from TLC and was used without further purification.

IR (nujol): 3400, 1740 cm^{-1}. NMR($CDCl_3$): δ 1·18 (t, 6 H, 2 CH_3), 2·20–2·40 (m, 1 H, $C\underline{H}{-}CH_3$), 5·40 (d, 1 H, CH–CN), 6·45 (s, 1 H, OH), 6·90 (d, 2 H, Ar), 7·96 (d, 2 H, Ar).

2.4. *4-(11-Undecenyloxy)-4′-cyanobiphenyl* **7**

A mixture of 4-hydroxy-4′-cyanobiphenyl (8·4 g, 42·9 mmol), 11-bromo-1-undecene (10·0 g, 42·9 mmol) and potassium carbonate (11·8 g, 85·8 mmol) in sieve-dried acetone (150 ml) was refluxed under anhydrous conditions for 48 h. Acetone was removed under reduced pressure, water added and the crude product was extracted into dichloromethane. The combined extracts were washed with water, dried ($MgSO_4$) and filtered. The solvent was removed from the filtrate and the crude product purified by flash chromatography on silica gel. Elution with dichloromethane–hexane (2 : 1) gave the desired product. Yield: 14·5 g, (97·4 per cent). The product gave one spot from TLC and was used without further purification.

IR (nujol): 2200 cm^{-1}. NMR ($CDCl_3$): δ 1·25–1·55 (m, 12 H, 6 CH_2), 1·75–1·90 (m, 2 H, $ArOCH_2C\underline{H}2$), 2·00–2·15 (m, 2 H, $CH_2{=}CHC\underline{H}_2$), 4·00 (t, 2 H, $ArOCH_2$), 4·90–5·07 (m, 2 H, $C\underline{H}_2{=}CH$), 5·70–5·95 (m, 1 H, $C\underline{H}_2{=}CH$), 6·99 (d, 2 H, Ar), 7·52 (d, 2 H, Ar), 7·62 (d, 2 H, Ar), 7·88 (d, 2 H, Ar).

2.5. *4-Carboxy-4′-(6-hexenyloxy)-biphenyl* **8b**

To a stirred alcoholic sodium hydroxide solution (2·1 g, 52·3 mmol), water (8 ml) and 95 per cent alcohol (13 ml) was added 6-bromo-1-hexene (4·26 g, 26·2 mmol) and 4-carboxy-4′-hydroxybiphenyl (5·0 g, 23·4 mmol) and the reaction mixture refluxed for 24 h. The reaction mixture was cooled and poured on to ice and the resulting precipitate filtered, washed with water and dried *in vacuo*. Recrystallization of the crude product from ethanol gave compound **8b**. Yield: 3·9 g (56·4 per cent); mp > 300°C.

IR (nujol): 1700 cm^{-1} NMR(DMSO): δ 1·45–1·60 (m, 2 H, CH_2), 1·70–1·85 (m, 2 H, CH_2), 2·05–2·20 (m, 2 H, $CH_2{=}CHC\underline{H}_2$), 4·03 t, 2 H, $ArOCH_2$), 4·94–5·12 (m, 2 H, $C\underline{H}_2{=}CH$), 5·73–5·97 (m, 1 H, $CH_2 = C\underline{H}$), 7·04 (d, 2 H, Ar), 7·67 (d, 2 H, Ar), 7·71 (d, 2 H, Ar), 7·99 (d, 2 H, Ar).

2.6. *4-Carboxy-4′-(4-butenyloxy)-biphenyl* **8a**

This compound was prepared in the same manner as compound **8b**. Yield: 47·6 per cent.

IR (nujol): 1680 cm^{-1}. NMR ($CDCl_3$): δ 2·50–2·65 (m, 2 H, CH_2), 4·07 (t, 2 H, $ArOCH_2$), 5·14 (t, 2 H, $C\underline{H}{=}CH$), 5·80–6·05 (m, 1 H, $CH_2{=}C\underline{H}$), 6·99 (d, 2 H, Ar), 7·58 (d, 2 H, Ar), 7·67 (d, 2 H, Ar), 8·06 (d, 2 H, Ar).

2.7. *4-Carboxy-4′-(8-octenyloxy)-biphenyl* **8c**

This compound was prepared in the same manner as compound **8b**. Yield: 48·2 per cent: mp 253·4°C.

IR (nujol): 1700 cm^{-1}. NMR ($CDCl_3$): δ 1·35–1·58 (m, 6 H, 3 CH_2), 1·72–1·88 (m, 2 H, $ArOCH_2C\underline{H}_2$), 2·00–2·15 (m, 2 H, $CH_2{=}CHC\underline{H}_2$), 3·99 (t, 2 H, $ArOCH_2$), 4·90–5·05 (m, 2 H, $C\underline{H}_2{=}CH$), 5·70–5·92 (m, 1 H, $CH_2{=}C\underline{H}$), 6·97 (d, 2 H, Ar), 7·56 (d, 2 H, Ar), 7·61 (d, 2 H, Ar), 8·07 (d, 2 H, Ar).

2.8. *4-Carboxy-4′-(11-undecenyloxy)-biphenyl* **8d**

This compound was prepared in the same manner as compound **8b**. Yield: 73·7 per cent; mp 242·5°C.

IR (nujol): 1700 cm^{-1}. NMR (DMSO): δ 1·20–1·50 (m, 12 H, 6 CH_2), 1·65–1·80 (m, 2 H, $ArOCH_2\underline{CH_2}$), 1·95–2·10 (m, 2 H, $CH_2{=}CH\underline{CH_2}$), 4·01 (t, 2 H, $ArOCH_2$), 4·90–5·05 (m, 2 H, $\underline{CH_2}{=}CH$), 5·70–5·90 (m, 1 H, $CH_2{=}\underline{CH}$), 7·04 (d, 2 H, Ar), 7·68 (d, 2 H, Ar), 7·74 (d, 2 H, Ar), 8·00 (d, 2 H, Ar).

2.9. *Preparation of monomer* **9b**

The acid **8b** (3·5 g, 11·8 mmol) was initially converted into the acid chloride by reacting with oxalyl chloride (3·0 g, 23·6 mmol) and sieve-dried dimethylformamide (2 drops) in sieve-dried benzene (30 ml) for 3 h at room temperature. The excess oxalyl chloride and the solvent were removed by distillation under reduced pressure. The crude acid chloride residue was dissolved in sieve-dried dichloromethane (15 ml) and added dropwise to a cold solution (0–5°C) of compound **6** (1·8 g, 8·2 mmol) and sieve-dried triethylamine (TEA) (1·5 ml) in sieve-dried dichloromethane (15 ml). The reaction mixture was stirred at room temperature overnight, washed with 5 per cent hydrochloric acid, water, dried ($MgSO_4$) and filtered. The solvent was removed from the filtrate and the remaining crude product was purified by column chromatography on silica gel (60–100 mesh). Elution with dichloromethane gave the pure product, which

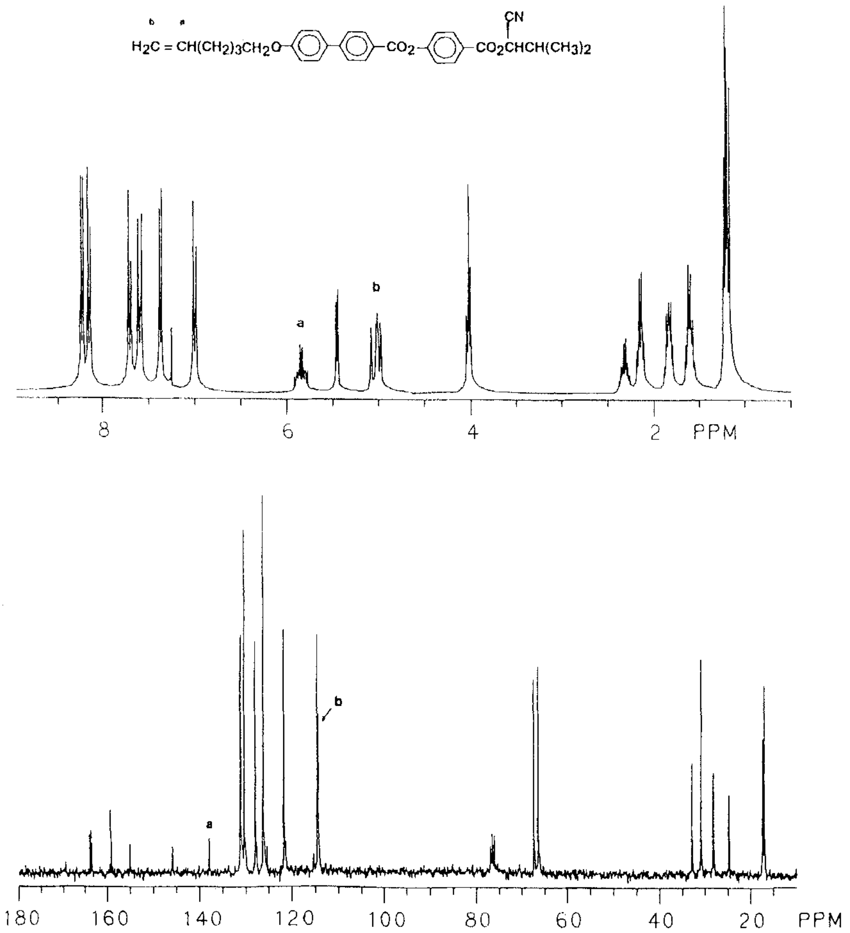


Figure 1. ^{1}H and ^{13}C NMR spectra of monomer **9b**.

was recrystallized from EtOH to give compound **9b**. Yield: 5·0 g (85·2 per cent); $[\alpha]_D^{25} = -11{\cdot}16°$ ($CHCl_3$). The ^1H and ^{13}C NMR spectra of compound **9b** are given in figure 1.

IR (nujol): 1730 cm^{-1}. NMR ($CDCl_3$): δ 1·20 (t, 6 H, 2 CH_3), 1·53 1·70 (m, 2 H, CH_2), 1·77–1·90 (m, 2 H, $ArOCH_2C\underline{H}_2$), 2·10–2·23 (m, 2 H, $CH_2{=}HC\underline{H}_2$), 2·28–2·42 (m, 1 H, $C\underline{H}CH_3$), 4·02 (t, 2 H, $ArOC\underline{H}_2$), 4·95–512 (m, 2 H, $C\underline{H}_2{=}CH$), 5·45 (d, 1 H, CH–CN), 5·75–5·97 (m, 1 H, $CH_2{=}C\underline{H}$), 7·00 (d, 2 H, Ar), 7·37 (d, 2 H, Ar), 7·60 d, 2 H, Ar), 7·70 (d, 2 H, Ar), 8·15 (d, 2 H, Ar), 8·23 (d, 2 H, Ar).

2.10. *Preparation of monomer* **9a**

This compound was prepared in the same manner as compound **9b**. Yield: 84·5 per cent.

IR (nujol): 1730 cm^{-1}. NMR ($CDCl_3$): δ 1·20 (t, 6 H, 2 CH_3), (m, 1 H, $C\underline{H}(CH_3)_2$), 2·52–2·65 (m, 2 H, $CH_2{=}CH{-}C\underline{H}_2$), 4·08 (t, 2 H, $ArOCH_2$), 5·10–5·24 (m, 2 H, $C\underline{H}_2{=}CH$), 5·45 (d, 1 H, CH–CN), 5·82–6·05 (m, 1 H, $CH_2{=}C\underline{H}$), 7·01 (d, 2 H, Ar), 7·37 (d, 2 H, Ar), 7·60 (d, 2 H, Ar), 7·70 (d, 2 H, Ar), 8·15 (d, 2 H, Ar), 8·23 (d, 2 H, Ar).

2.11. *Preparation of monomer* **9c**

This compound was prepared in the same manner as compound **9b**. Yield: 85·0 per cent; $[\alpha]_D^{25} = -10{\cdot}04°$ ($CHCl_3$).

IR (nujol): 1730, 1720 cm^{-1}. NMR ($CDCl_3$): δ 1·20 (t, 6 H, 2 CH_3), 1·35–1·60 (m, 6 H, 3CH_2), 1·75–1·90 (m, 2 H, $ArOCH_2C\underline{H}_2$), 2·00–2·17 (m, 2 H, $CH_2{=}CHC\underline{H}_2$), 2·24–2·43 (m, 1 H, $C\underline{H}{-}CH_3$), 4·01 (t, 2 H, $ArOCH_2$), 4·92–5·08 (m, 2 H, $C\underline{H}_2{=}CH$), 5·45 (d, 1 H, CH–CN), 5·73–5·95 (m, 1 H, $CH_2{=}C\underline{H}$), 7·00 (d, 2 H, Ar), 7·37 (d, 2 H, Ar), 7·60 (d, 2 H, Ar), 7·70 (d, 2 H, Ar), 8·15 (d, 2 H, Ar), 8·23 (d, 2 H, Ar).

2.12. *Preparation of monomer* **9d**

This compound was prepared in the same manner as compound **9b**. Yield 75·4 per cent $[\alpha]_D^{25} = -8{\cdot}73°$ ($CHCl_3$).

IR (nujol): 1735, 1725 cm^{-1}. NMR ($CDCl_3$) δ 1·20 (t, 6 H, 2 CH_3), 1·30–1·60 (m, 12 H, 6 CH_2), 1·75–1·90 (m, 2 H, $ArOCH_2C\underline{H}_2$), 2·00–2·14 (m, 2 H, $CH_2{=}CHC\underline{H}_2$), 2·20–2·42 (m, 1 H, $C\underline{H}{-}CH_3$), 4·01 (t, 2 H, $ArOCH_2$), 4·90–5·08 (m, 2 H, $C\underline{H}_2{=}CH$), 5·45 (d, 1 H, CH–CN), 5·70–5·95 (m, 1 H, $CH_2{=}C\underline{H}$), 7·00 (d, 2 H, Ar), 7·37 (d, 2 H, Ar), 7·59, (d, 2 H, Ar), 7·70 (d, 2 H, Ar), 8·15 (d, 2 H, Ar), 8·23 (d, 2 H, Ar).

2.13. *Synthesis of polymers* **10a–d**

A stirred mixture of monomer **9** (1·0 mmol), polymethylhydrosiloxane (0·9 mmol), 5 per cent hexachloroplatinic acid in isopropanol (2 drops) and sodium-dried toluene (5 ml) was heated under nitrogen and anhydrous conditions at 110°C for 24 h. The solvent was removed under reduced pressure and the crude polymer purified by precipitation from solution in dichloromethane by the addition of petroleum ether or methanol. The polymer was isolated by centrifugation and this procedure repeated until the product shown to be free from alkene by TLC. The ^1H and ^{13}C NMR spectra of polymer **10b** are given in figure 2.

2.14. *Synthesis of copolymers* **11a–c** *and* **12**

The copolymerization was carried out in the same manner except using different percentages from compounds **9** and **7** to give copolymers **11a–c** or using 70 per cent dimethyl and 30 per cent methylhydrosiloxanes to give copolymer **12**.

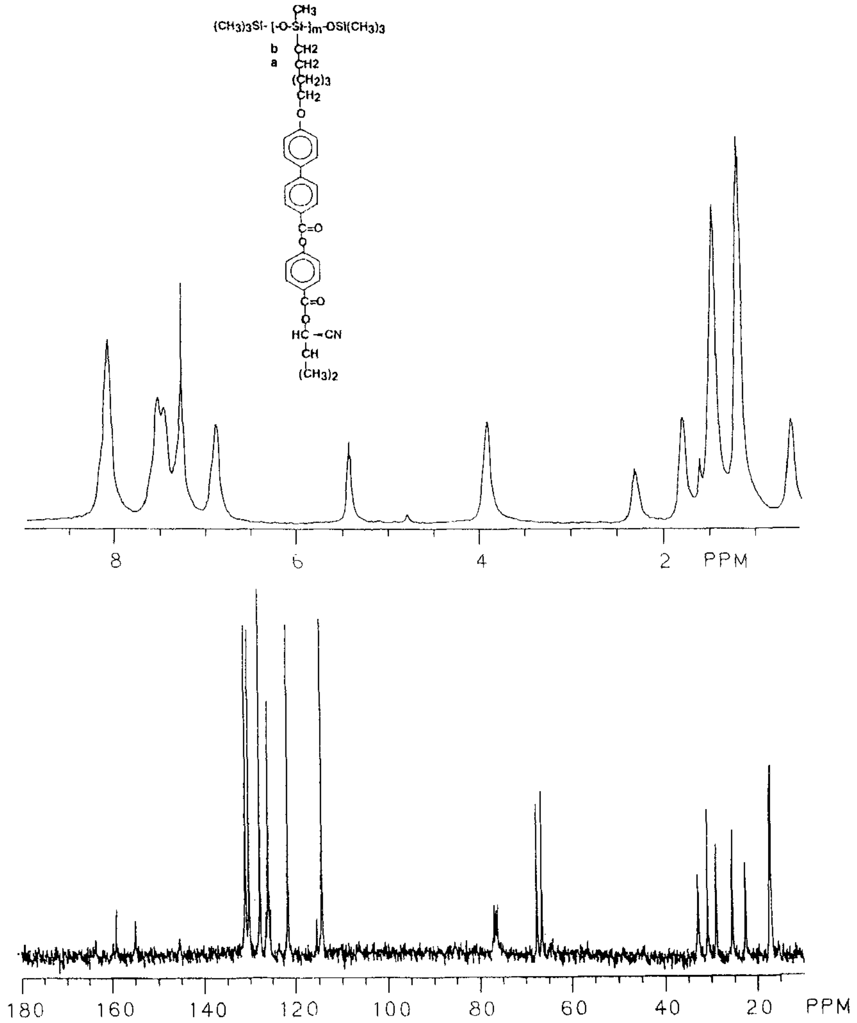


Figure 2. ^1H and ^{13}C NMR spectra of polymer **10b**.

3. Results

3.1. *Liquid crystalline behaviour of the monomers*

The transition temperatures of the vinyl monomers with a cyanohydrin ester as the chiral centre are given in table 1. All the synthesized vinyl moieties have the mesomorphic sequence $I \rightarrow S_A \rightarrow S_C^* \rightarrow C$. However, only monomer **9b** with methylene unit $n=4$ has a chiral nematic phase. The transition temperatures of the vinyl moieties decrease with increase of the length of the spacer. Microscopic studies showed that the ferroelectric S_C^* phase appeared with a striated focal-conic texture on cooling from the S_A phase. A typical focal-conic texture of the smectic A phase of vinyl monomer **9b** is shown in figure 3. The broken focal-conic fan texture of the S_C^* phase of vinyl monomer **9b** on cooling from the S_A phase is shown in figure 4. Monomer **9b** also shows the chiral nematic phase on cooling from the isotropic liquid (see figure 5). The thermal properties of these monomers were studied using a DSC-7 Perkin–Elmer apparatus at $10°C\,min^{-1}$ on heating and cooling. The thermogram of monomer **9b** is shown in figure 6.

Table 1. Transition temperatures (°C) of monomers **9a–d.**

Monomer	*n*	C	S_C^*	S_A	N*	I
9a	2	129·4	156·5	168·0	—	169·3
9b	4	91·2	116·1	145·0	154·4	156·1
9c	6	54·6	98·0	136·6	—	145·3
9d	9	40·8	75·9	125·9	—	138·7

Figure 3. A typical focal-conic texture of the smectic A phase of monomer **9b**.

Figure 4. The broken focal-conic fan texture of the smectic C* phase of monomer **9b**.

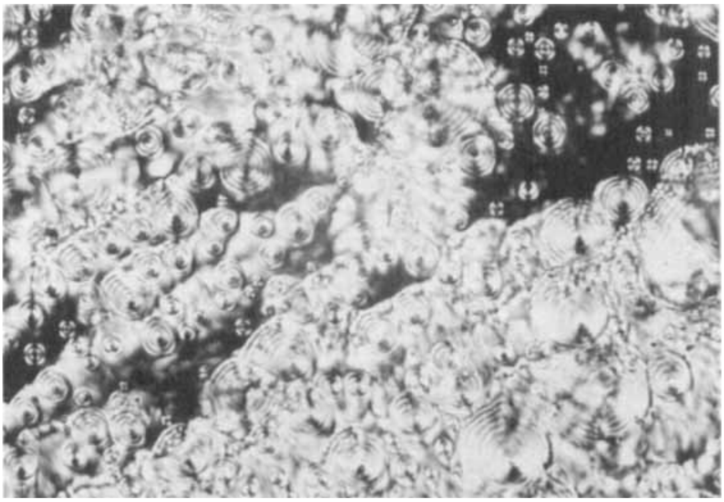


Figure 5. The chiral nematic texture of monomer **9b**.

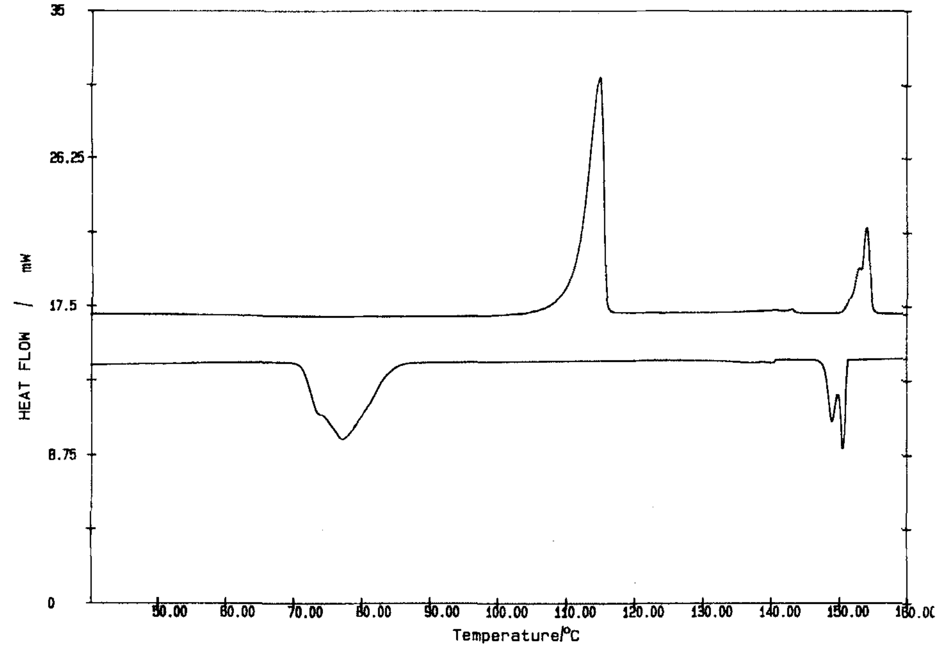


Figure 6. The DSC curves of monomer **9b**.

3.2. *Liquid crystalline behaviour of the polymers*

The transition temperatures and the polymerization data of the homo and copolysiloxanes are reported in tables 2 and 3. The degree of polymerization for all the polymers is in the range from 30 to 35 and the polydispersity is from 1·6 to 3·0. The mesomorphic behaviours of all the polymers are tentatively assigned by optical microscopy and DSC. Polymer **10a**, with short spacer, exhibits the bâtonnets of the smectic A phase on cooling from the isotropic liquid (see figure 7). Below the smectic A phase, the S_C^* phase appeared with a broken focal-conic fan texture. Polymers **10b** and

Table 2. Transition temperatures (°C) and molecular weights of polymers **10a–d.**

Polymer	n	M_n	γ	Transition temperatures
10a	2	15300	1·9	g 47·5 T_1 106 S_C^* 174·9 S_A 230·3 I
10b	4	13000	2·8	g 37·1 S_C^* 185·1 N* 257·9 I
10c	6	28000	1·6	C 48·9 S_C^* 177·3 N* 275·6 I
10d	9	16800	2·1	g 39·0 N* 271·7 I

M_n, number average molecular weight; γ, polydispersity.

Table 3. Transition temperatures and molecular weights of copolymers **11a–c** and **12.**

Polymer	x	y	z	M_n	γ	Transition temperatures
11a	5	95	—	13000	2·5	g 4·2 S_C^* 154·9 I
11b	50	50	—	15000	3·0	g 17·2 T_1 43·2 S_C^* 215 I
11c	75	25	—	16400	2·1	C 78·1 S_C^* 249·7 I
12	33·3	—	66·7	8400	1·6	C 56·9 S_C^* 196·7 I

M_n, number average molecular weight; γ, polydispersity.

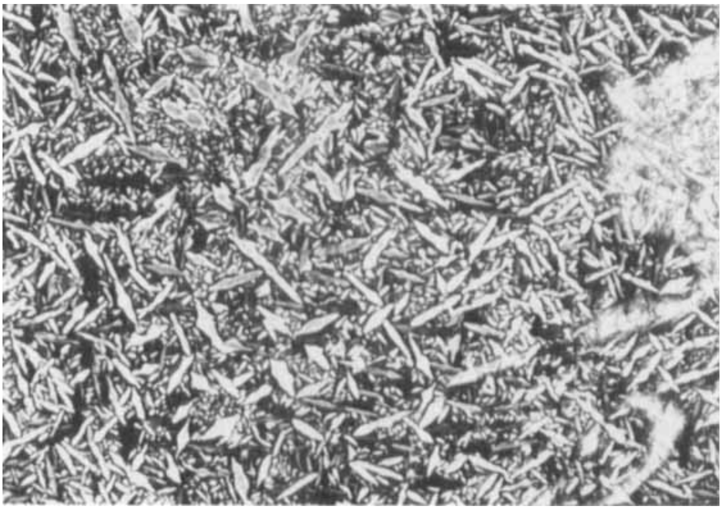


Figure 7. The bâtonnets of the smectic A phase of polymer **10a**.

10c present both the S_C^* and chiral nematic phases. Only a chiral nematic phase is observed for polymer **10d**. All the sidechain and mainchain copolysiloxanes present the ferroelectric S_C^* phase with a very broad temperature range. These polymers have no chiral nematic and smectic A phases. A photomicrograph of the S_C^* texture of copolymer **11a** is shown in figure 8.

The DSC analysis of the ferroelectric liquid crystalline polysiloxanes was performed with a heating and cooling rate of 20°C min^{-1}. The transition temperatures were determined on heating. These studies confirmed that all the synthesized polysiloxanes have enantiotropic mesophases. Some of the polymers exhibit crystalline character.

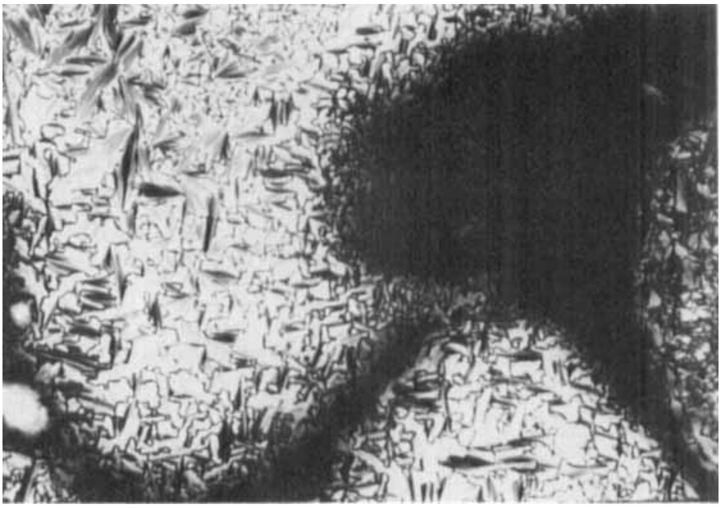


Figure 8. The photomicrograph of the smectic C* phase of copolymer **11a**.

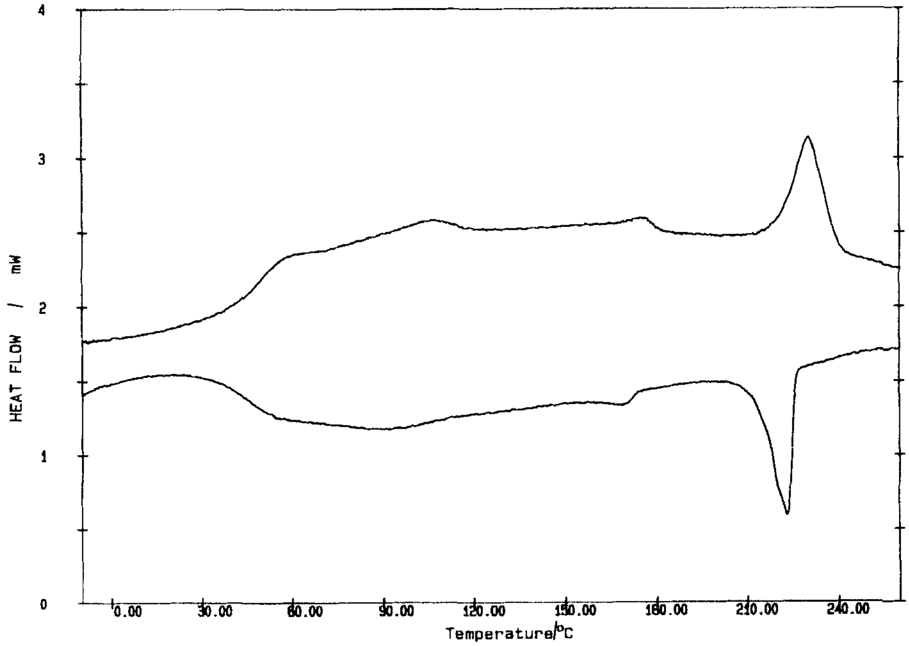


Figure 9. The DSC curves of polymer **10a**.

The glass transition temperatures of the homopolymers, measured to be the temperature at which the DSC curve is halfway between the extrapolated tangents to the baselines above and below the glass transition region, decrease with increasing spacer length. The glass transition temperatures of the copolymers increase with increase of the concentration of the chiral mesogen **9d**. The dilution effect of the cyanobiphenyl vinyl moiety seems to favour the formation of the S_C^* phase. DSC thermograms of polysiloxanes **10a** and **10d** are shown in figures 9 and 10.

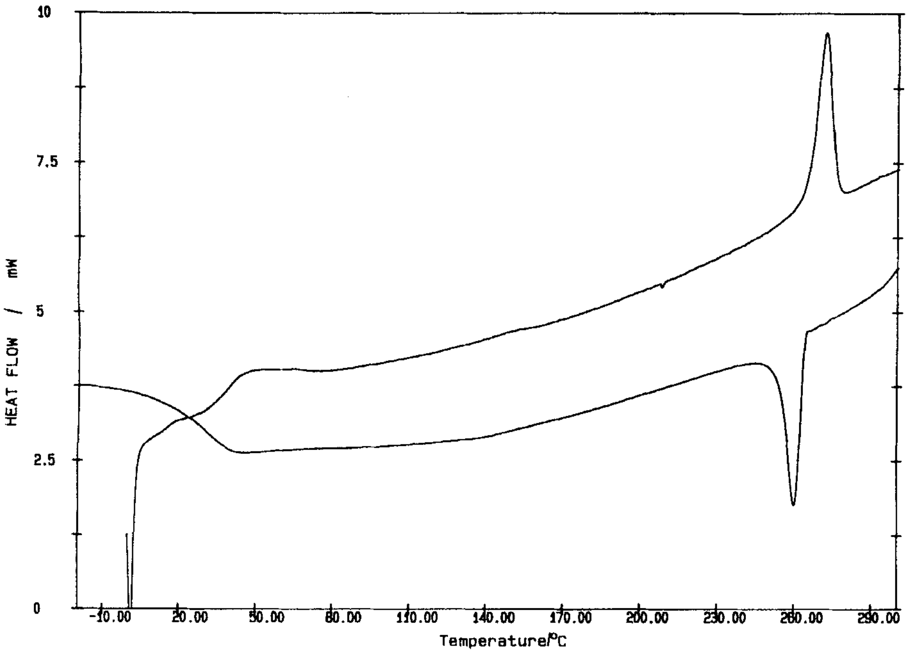


Figure 10. The DSC curves of polymer **10d**.

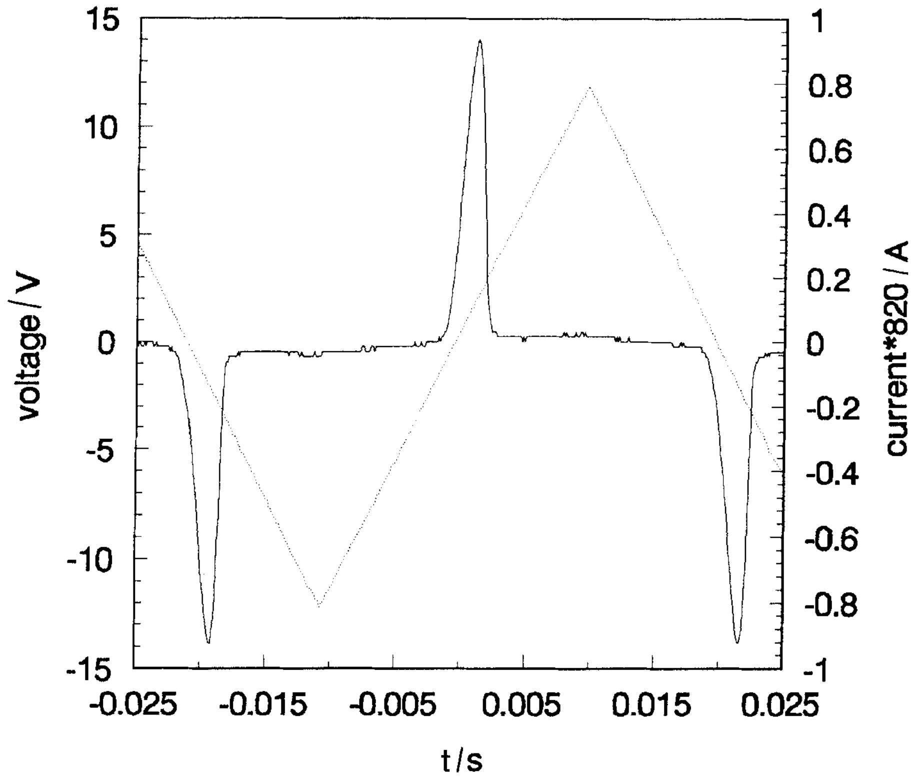


Figure 11. The plot of a voltage–time and current–time function at a temperature of 97·7°C. …, Voltage; —, current*820.

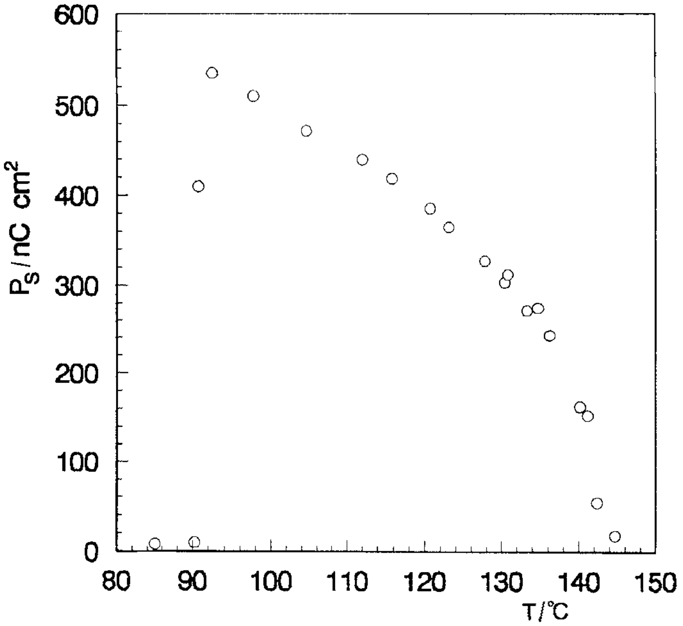


Figure 12. The calculated spontaneous polarization as a function of temperature.

4. Spontaneous polarization and tilt angle

We report here observations carried out with monomer **9b**. Measurements were made on a 5 μm thick sample of area of $1{\cdot}4 \times 15\,\mathrm{cm}^2$ sandwiched between two glass sides. The inner surfaces were coated with ITO. The liquid crystal was aligned homeotropically in the smectic A phase and on cooling a homeotropic smectic C* texture with horizontal layers was obtained. The texture was then transformed to a bookshelf texture with the polarization direction vertical to the film [6] by application of an 8 V pulse.

The measurement of the spontaneous polarization was carried out on films in the bookshelf texture. A triangular voltage (amplitude of 12 V, frequency 25 Hz) was applied and the current monitored by measuring the voltage drop across a resistance of 820 Ω, using a HP digital oscilloscope 54601A. Figure 11 shows a typical result. The spontaneous polarization can be derived from the polarization current $A{\cdot}\partial P/\partial t$ (A = area of the LC film) that is due to the field induced reversal of the polarization. The reversal polarization occurs suddenly and results in a surge of the polarization current represented by the peaks in the current versus time curve of figure 11. The area under the peaks is proportional to P_s ($I = 2AP_s$). The derived spontaneous polarization are shown in figure 12 as a function of temperature. The spontaneous polarization is relatively large. It reaches values of more than 500 nC/cm^2.

Films with uniform bookshelf textures are needed for the measurements of the tilt angle. They were obtained from the homeotropic smectic C* texture by shearing the film gently during the field induced transition to the bookshelf texture [6]. With the spontaneous polarization parallel to a vertical field the director is in the plane of the film and forms the tilt angle θ with the layer normal. When the field and polarization are reversed, the director rotates to the other side ($\theta \rightarrow -\theta$) but the layer orientation remains unchanged. The directions of extinction for a sample between crossed

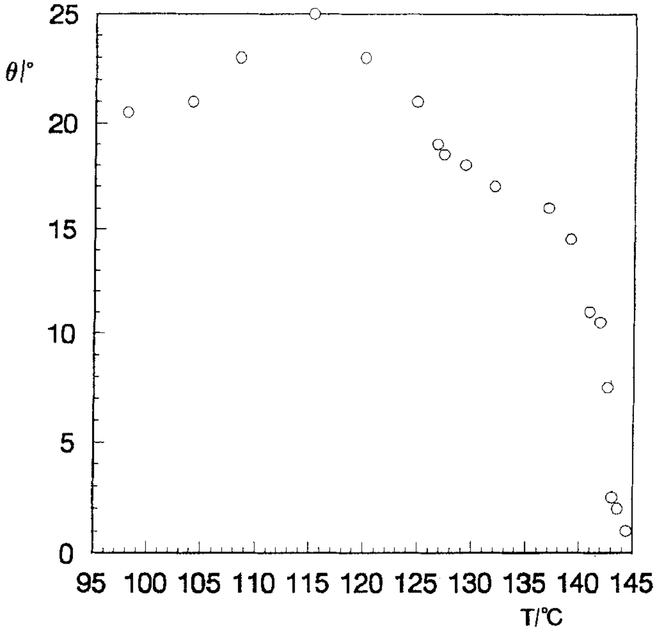


Figure 13. The tilt angle as the function of temperature.

polarizers change during this process also by 2θ. The tilt angle can be, therefore, easily measured optically.

Results for the temperature dependence of the tilt angle are shown in figure 13. The temperature dependence of the tilt angle and the polarization shows the expected critical behaviour near the smectic A–smectic C transition which appears to be second order. Close to the transition the polarization and tilt angle are proportional but at lower temperature they behave differently. The tilt angle reaches a maximum at 115°C while the polarization increases with decreasing temperature over the total smectic C* range. However, it should be kept in mind that the error in the tilt angle measurement of $\pm 3°$ is relatively large and that some of the observed deviation may not be real. The temperature behaviour is unusual and may be connected with the fact that the material has a strong spontaneous polarization.

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