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Ferroelectric liquid crystalline side group polymers derived from mesogenic vinyl ether monomers†

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Two classes of ferroelectric polymers, polysiloxanes and polyvinyl ethers, have been synthesized, starting from the same mesogenic vinyl ether as precursor. The polysiloxane materials obtained by polymer analogous reaction of vinyl ethers with H-siloxanes exhibit larger ranges of ferroelectric S_C^* phases than the corresponding polyvinyl ethers. The effect of changing the nature of the link of the terminal chiral end group on the phase behaviour and ferroelectric properties of the new side chain polymers is reported.

1. Introduction

Polymeric ferroelectric liquid crystals (PFLCs) have been investigated for use in large area displays because they combine features of a polymer material with the favourable properties of low molar mass FLCs [1, 2]. However, there are several difficulties to overcome for the practical application of PFLCs. Most polymers have slow responses in an electric field and their orientation in cells is problematical. Shibaev *et al.*, were the first to report a ferroelectric liquid crystal polymer [3], and the first report of electro-optical switching in a PFLC came from Uchida *et al.* [4]. Since that time, a number of switchable PFLCs have been designed and studied by many researchers [5].

Our goal was to synthesize new polysiloxanes and polyvinyl ethers derived from mesogenic vinyl ethers. One example of grafting of a chiral mesogenic vinyl ether on to a poly(hydrogenmethylsiloxane) has recently been reported by Chiellini *et al.* [6]. This polymer exhibited S_A and S_C^* phases. Ferroelectric properties and electro-optical investigations were not described.

We have designed vinyl ether monomers with a mesogenic part consisting of three aromatic rings and terminally linked to a chiral moiety derived from lactic acid. Between the vinyl ether group and the mesogenic unit, a spacer of ten methylene groups was placed. The polyvinyl ethers were obtained via cationic polymerization and the polysiloxanes by polymer analogous reaction between H-siloxanes and vinyl ether monomers.

We have investigated the influence of the type of polymer backbone on the liquid crystalline behaviour. As a result we found that polysiloxanes show more favourable ferroelectric behaviour, for example, higher spontaneous polarization and electro-optical switching over a broader temperature range than the polyvinyl ethers. Furthermore we observed that the local environment of the chiral centre is extremely important for the ferroelectric properties.

2. Experimental

2.1. *Synthesis*

The molecular structures of the polyvinyl ethers and polysiloxanes are shown in figure 1.

The synthesis of vinyl ether **7** as precursor for polyvinyl ether **PVE-1** and polysiloxane **PS-1** is given as an example in scheme 1.

The etherification reaction of THP-protected 10-bromodecanol, **2** with 4-hydroxybiphenyl-4′-carboxylic acid, **3** in the presence of KOH, and subsequent hydrolysis by concentrated hydrochloric acid in THF gave the 4-(10-hydroxydecyloxy)biphenyl-4′-carboxylic acid **4**. The vinyl ether **5** was obtained by palladium-catalysed reaction of *n*-butylvinyl ether with compound **4** [7]. The chiral phenol ester **6** was synthesized by coupling *S*-butyl lactate with 4-benzyloxy benzoic acid under standard Steglich conditions [9] and subsequent deprotection by hydrogenolysis catalysed by palladium on activated carbon. The target mesogenic vinyl ether **7** was prepared by esterification of carboxylic acid **5** with compound **6** [9]. **7** was purified by column chromatography on silica gel and by recrystallization for diethyl ether. The other monomers **8** and **9** (figure 2) were synthesized in an analogous manner

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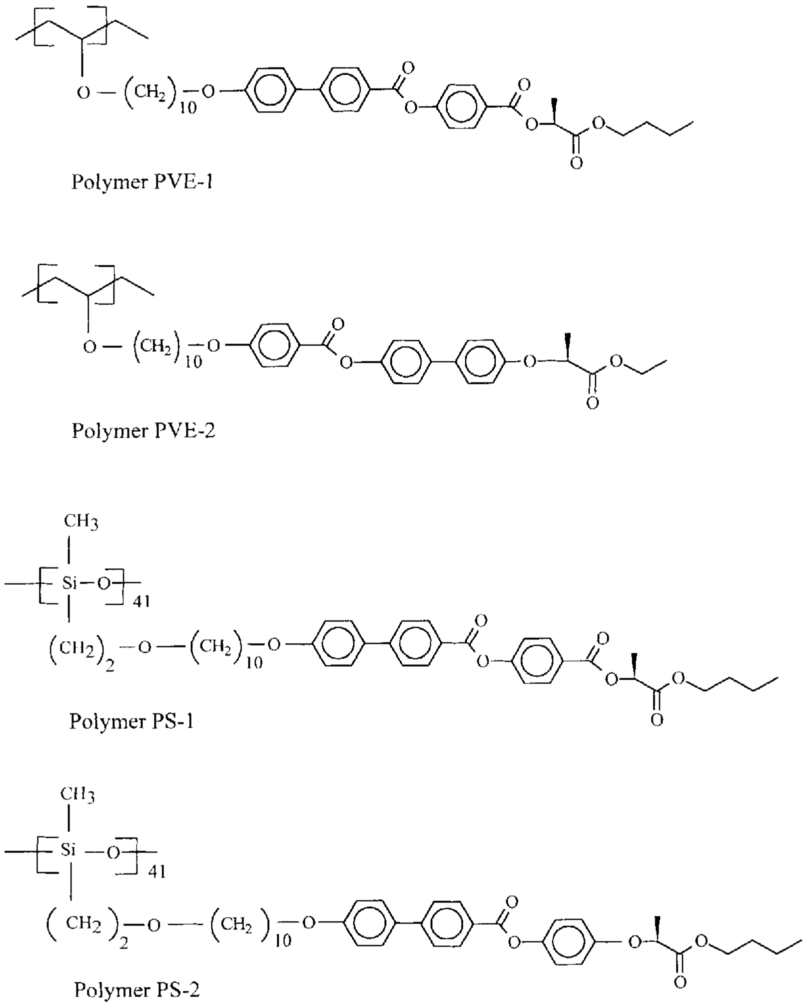


Polymer PVE-1

Polymer PVE-2

Polymer PS-1

Polymer PS-2

Figure 1. Molecular structures of polyvinyl ethers and polysiloxanes.

except for the lactic acid, which was attached via Mitsunobu reaction [8].

The polyvinyl ethers (oligomers) were synthesized *via* cationic polymerization using trifluoromethylsulphonic acid/dimethyl sulphide (DMS) as catalyst [7] (see scheme 2).

The polysiloxanes **PS-1** and **PS-2** were obtained through the hydrosilylation reaction of the H-siloxane and the vinyl ether monomers in the presence of platinum divinyltetramethyldisiloxane (DVTMS) [6], as shown in scheme 2.

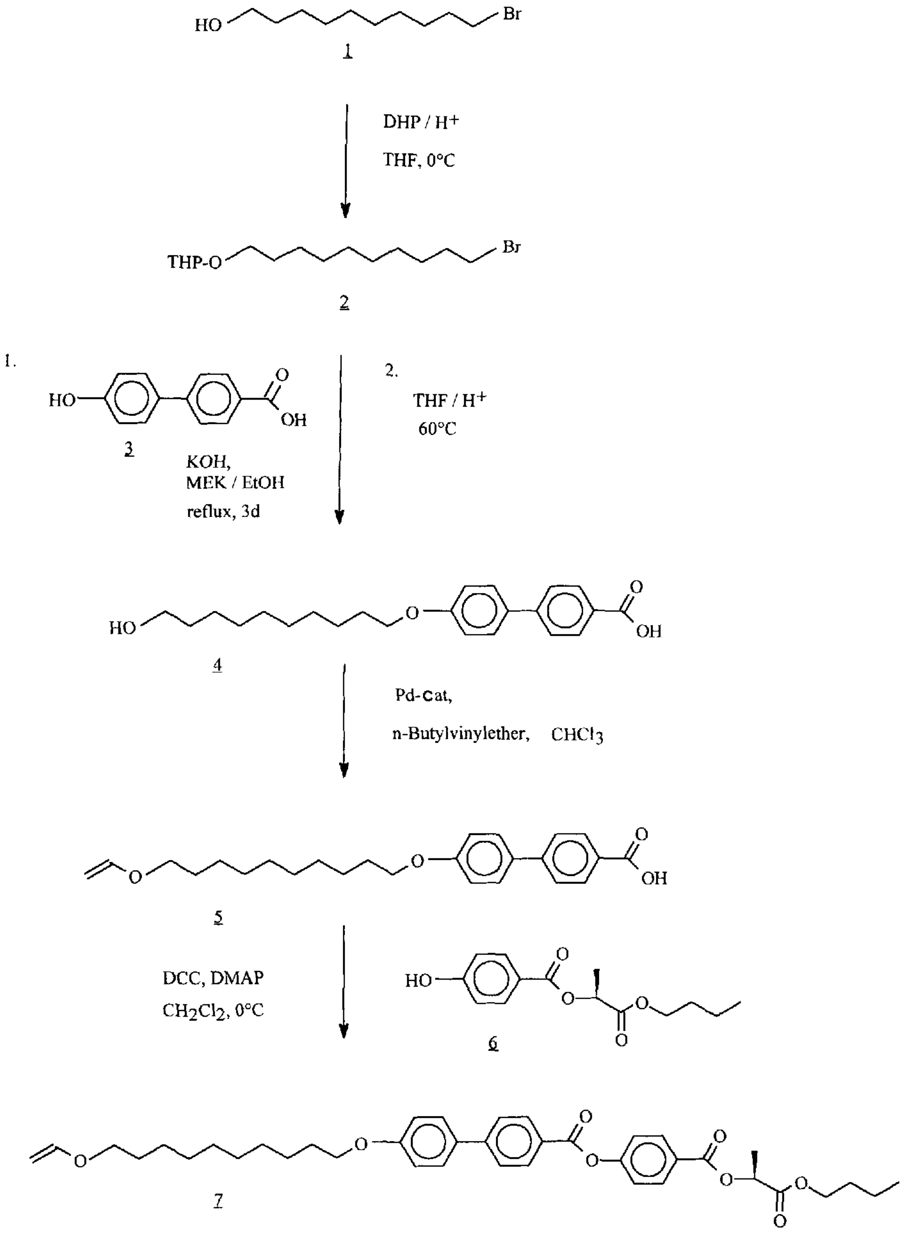
2.2. *Analytical data*

2.2.1. *Vinyl ether monomer* 7

IR (KBr) ν/[cm^{-1}]: 2933, 2857 (C–H), 1730 (C=O), 1605, 1497 (Ar), 1260, 1162 (C–O). MS *m/z*: 645 (M +), 572 ($C_{35}H_{39}O_7$), 379 ($C_{25}H_{31}O_3$), 197 ($C_{13}H_9O_2$). ^{1}H NMR ($CDCl_3$): δ = 0·92 (t, J = 7 Hz, 3 H), 1·25–1·52 (m, 16 H), 1·65 (d, J = 7 Hz, 3 H), 1·65 (quint, J = 7 Hz, 2 H), 1·82 (quint, J = 7 Hz, 2 H), 3·67 (t, J = 7 Hz, 2 H), 3·97 (dd, J = 7 and 2 Hz, 1 H), 4·01 (t, J = 7 Hz, 2 H), 4·18, 4·20 (ABt, J = 14 and 2 Hz, 1 H), 4·19 (ABt, J = 14 and 7 Hz, 2 H), 5·34 (q, J = 7 Hz, 1 H), 6·47 (dd, J = 14 and 7 Hz, 1 H) 7·00, 7·60 (AA′BB′, J = 8·5 Hz, 4 H), 7·34, 8·24 (AA′BB′, J = 8·5 Hz, 4 H), 7·70, 8·18 (AA′BB′; J = 8·5 Hz, 4 H).

2.2.2. *Vinyl ether monomer* 8

IR (KBr) ν/[cm^{-1}]: 2935, 2858 (C–H), 1731 (C=O), 1605, 1496 (Ar), 1256, 1165 (C–O). MS *m/z*: 588 (M +), 303 ($C_{19}H_{27}O_3$), 286 ($C_{17}H_{18}O_4$), 259 ($C_{17}H_{23}O_2$), 91 (C_7H_7). ^{1}H NMR ($CDCl_3$): δ = 1·27 (t, J = 7 Hz, 3 H), 1·30–1·52 (m, 12 H), 1·65 (d, J = 7 Hz, 3 H), 1·65 (quint, J = 7 Hz, 2 H), 1·82 (quint, J = 7 Hz, 2 H), 3·67 (t, J = 6·5 Hz, 2 H), 3·97 (dd, J = 7 and 2 Hz, 1 H), 4·05 (t, J = 6·5 Hz, 2 H). 4·16 (dd, J = 14 and 2 Hz, 1 H), 4·24 (q, J = 7 Hz, 2 H), 4·79 (q, J = 7 Hz, 1 H), 6·47 (dd, J = 14 and 6·5 Hz, 1 H), 6·95, 8·15 (AA′BB′, J = 9 Hz, 4 H), 6·97, 7·49 (AA′BB′, J = 9 Hz, 4 H), 7·24, 7·56 (AA′BB′, J = 9 Hz, 4 H).



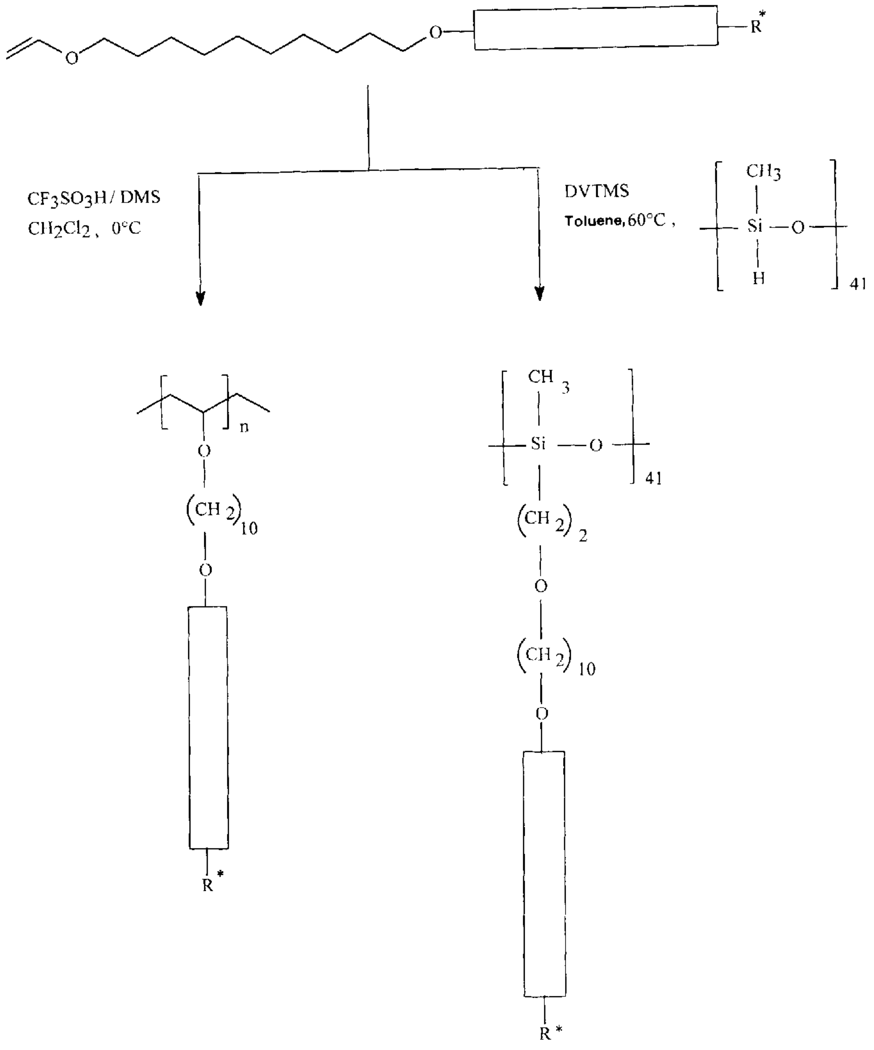
Scheme 1. Synthesis of mesogenic vinyl ether monomer.

2.2.3. *Vinyl ether monomer 9*

IR (Kbr) ν/[cm^{-1}]: 2935, 2857 (C–H), 1730 (C=O), 1605, 1498 (Ar), 1254, 1165 (C–O). MS *m/z*: 616 (M +), 379 ($C_{25}H_{31}O_3$), 197 ($C_{13}H_9O_2$). ^{1}H NMR ($CDCl_3$): δ = 0·91 (t, J = 7 Hz, 3 H), 1·28–1·52 (m, 14 H), 1·63 (quint, J = 7 Hz, 2 H), 1·63 (d, J = 7 Hz, 3 H), 1·65 (quint, J = 7 Hz, 2 H), 1·81 (quint, J = 7 Hz, 2 H), 3·67 (t, J = 6·5 Hz, 2 H), 3·97 (dd, J = 7 and 2 Hz, 1 H), 4·01 (t, J = 6·5 Hz, 2 H), 4·16 (dd, J = 14 and 2 Hz, 1 H), 4·16, 4·18 (ABt, J = 14·5 and 7 Hz, 2 H), 4·75 (q, J = 7 Hz, 1 H), 6·46 (dd, J = 14 and 7 Hz, 1 H), 6·92, 7·13 (AA′BB′, J = 9 Hz, 4 H), 7·00, 7·59 (AA′BB′, J = 9 Hz, 4 H), 7·67, 8·21 (AA′BB′, J = 9 Hz, 4 H).

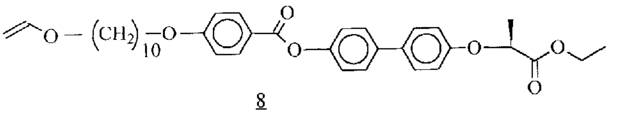
2.3. *Physical methods*

The structural assignment of each compound synthesized was determined by ^{1}H NMR, MS and IR spectroscopy. Molecular weights were measured by gel permeation chromatography using 2PL-gel columns, tetrahydrofuran as eluent and polystyrene as standard. The phase transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin–Elmer DCS7 apparatus at a scanning rate of 5 K min^{-1}, and the phases were identified using polarizing optical microscopy and 4–10 μm thick polyimide coated cells. The spontaneous polarizations were measured by triangular wave method [10]. X-ray diffraction was carried out using



Scheme 2. Synthesis of polymers.

a vacuum chamber with a flat film camera at a distance of 81 mm from the sample. Monochromatic CuK$_\alpha$ radiation ($\lambda = 0{\cdot}15418$ nm, graphite monochromator) was focused by a glass capillary. The polymer sample was oriented inside the chamber in a magnetic field (2·4 Tesla) perpendicular to the incident beam.



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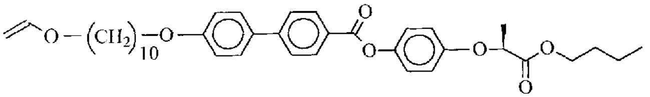

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Figure 2. Molecular structures of monomers **8** and **9**.

3. Results and discussion

We have synthesized four polymers, two polyvinyl ethers (**PVE-1** and **PVE-2**) and two polysiloxanes (**PS-1** and **PS-2**) and compare the phase behaviours and ferroelectric properties as a function of the polymer backbone and the chiral moieties. Comparison of the molecular weights shows that the cationic polymerization affords only oligomers (see table 1). The polysiloxanes were obtained in good yields (50–60 per cent).

Table 1. Molar mass and weight distributions for the polymers.

Polymer	M_w/g mol^{-1}	M_w/M_n
PVE-1	4800	1·5
PVE-2	4200	1·4
PS-1	22400	1·6
PS-2	21500	1·9

Table 2. Phase transition temperatures and spontaneous polarizations of the polymers.

Polymer	Phase transitions/°C	P_s/nC cm^{-2}
PVE-1	Cr 70 S_A 179 I	—
PVE-2	Cr 65 S_C^* 82 S_A 112 I	32
PS-1	Cr 23 S_C^* 175 S_A 234 I	44
PS-2	T_g 28 S_F/S_I 50 S_{CX}^* 95 S_{CY}^* 140 S_A 182 I	155

The phase transition temperatures of the polymers are given in table 2.

Three polymers exhibit both smectic C* and smectic A phases. Polyvinyl ether **PVE-1** which has no S_C^* phase shows electroclinic switching in the S_A phase over the temperature range of 100°C, with switching times below 1 ms above 140°C—see figure 3. **PVE-2**, which has an ether linkage between the mesogenic core and the chiral moiety and the phenyl- and biphenyl-parts of the core interchanged, with respect to **PVE-1**, exhibits a 15°C broad S_C^* phase with $P_S = 32\,\mathrm{nC\,cm^{-2}}$ as the maximum—see figure 4. The decrease of P_S at temperatures below 68°C may be due to the increasing viscosity. A second consequence of the modified mesogen, i.e. moiety, is a distinct shift of the isotropic to smectic phase transition to lower temperatures, as shown in table 2.

Polysiloxane **PS-1** has a broad smectic C* phase which ranges from room temperature up to 175°C. The temperature dependence of the spontaneous polarization is demonstrated in figure 5. The unusual drop in the spontaneous polarization of **PS-1** with decreasing temperature has also been observed in other cases [4, 11].

PS-2 shows two smectic C* phases, S_X and S_Y. At their transition, a distinct jump in the spontaneous polarization occurs. For a detailed mesophase assignment, X-ray diffraction measurements on a magnetically oriented sample at different temperatures were made. Due to the magnetic moment of the phenyl rings, the side groups are oriented parallel to the magnetic field. For the S_A phase, a layer periodicity $d = 4{\cdot}21\,\mathrm{nm}$, corresponding to a monolayer arrangement of S_{A1} type was found. Perpendicular to the layer reflection (up to the third order), diffuse crescents due to the lateral liquid-like arrangement of the side groups are observed ($D = 0{\cdot}522\,\mathrm{nm}$).

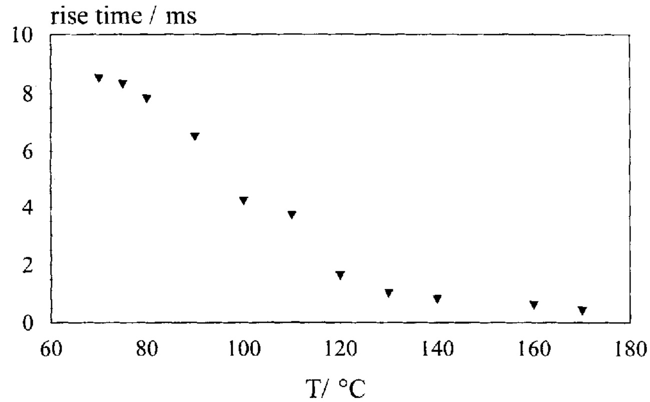

Figure 3. Temperature dependence of switching time for **PVE-1** in its S_A phase.

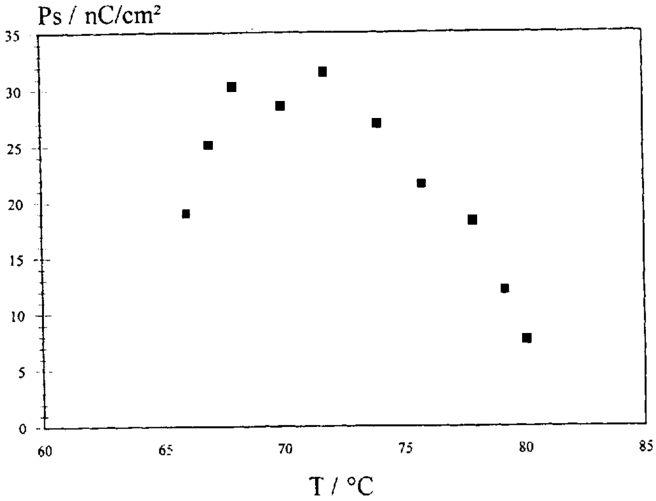

Figure 4. Temperature dependence of the spontaneous polarization for **PVE-2**.

For the S_{CY}^* phase, which occurs from 95 to 140°C, a layer periodicity $d = 4{\cdot}09\,\mathrm{nm}$ at 121°C and a lateral spacing of the mesogens of $D = 0{\cdot}507\,\mathrm{nm}$ was determined. For the S_{CX}^* phase, which exists between 50 and 95°C, a layer periodicity $d = 4{\cdot}00\,\mathrm{nm}$ and a lateral separation $D = 0{\cdot}502\,\mathrm{nm}$ were found. In this phase, an additional diffuse reflection having a periodicity of 0·9 nm was observed, this can be assigned to a periodicity of siloxanes.

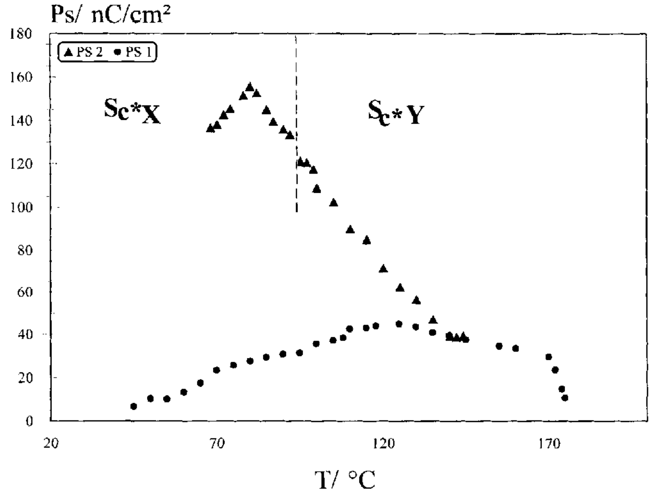

Figure 5. Temperature dependence of the spontaneous polarization from **PS-1** and **PS-2**.

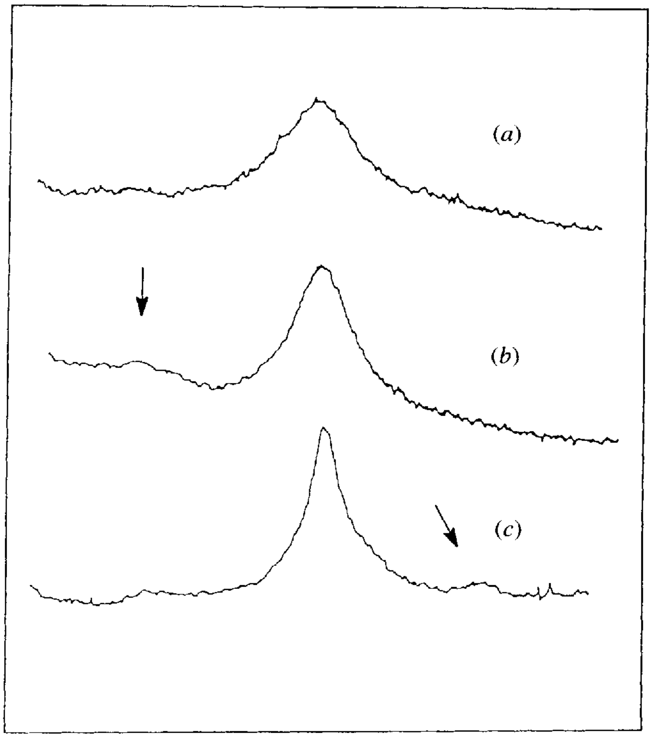

Figure 6. Densitometer scans of X-ray patterns of an oriented sample **PS-2** perpendicular to the magnetic field (4° to 32° 2θ). (*a*) 121°C S^*_{CY}, (*b*) 75°C S^*_{CX}, (*c*) 18°C S_F/S_I. Half width for (*a*) $\Delta\ (2\theta) = 4{\cdot}3°$ (FWHM), for (*b*) $\Delta\ (2\theta) = 3{\cdot}3°$ (FWHIM) and for (*c*) $\Delta\ (2\theta) = 2{\cdot}0°$ (FWHM).

Because of the monolayer arrangement (total overlapping of side groups), the periodicity of siloxanes should be approximately twice the lateral spacing.

The main difference between the S^*_C phases is the decrease of the half width of the wide angle crescents (see figure 6 (*a*) and (*b*)). For the S^*_{CY} phase, a value of 4·3° (FWHM in 2θ) and for the S^*_{CX} phase of 3·3°C (FWHM in 2θ) was determined. These are typical values for S_A/S_C phases [12]. The smaller half width in the case of the S^*_{CX} phase corresponds to smaller variations in the lateral distance between mesogenic moieties. Below the two smectic C* phases, another tilted smectic phase with a layer periodicity $d = 4{\cdot}13$ nm and a lateral separation of mesogenic units $D = 0{\cdot}492$ nm exists. The half width of the wide angle crescent of 2·0° is greater than the value of 0·75° normally found for S_B phases [13], but distinctly smaller compared to values for S_A/S_C phases. Therefore this phases can be assigned as S_F/S_I phase—see figure 6 (*c*). In this figure, a second order reflection which has a periodicity of 0·353 nm can be observed. The ratio of first to second order reflection is 1·4. This value corresponds better to a value of $2^{\frac{1}{2}}$ than $3^{\frac{1}{2}}$. For this reason, we assume a two dimensional rectangular lateral arrangement of the mesogenic units.

It is remarkable that the replacement of the ester linkage between the mesogen unit and the chiral moiety (**PS-1**) by an ether linkage (**PS-2**) leads to a smaller S^*_C phase range, consisting of two sub-phases, to the occurrence of a S_F/S_I phase, and to a decrease of the S_A to isotropic phase transition temperature.

The link between the chiral centre and the core has also an important influence on the spontaneous polarization. **PS-2** having the chiral centre located nearer to the aromatic core shows a much higher spontaneous polarization ($155\,\mathrm{nC\,cm^{-2}}$) than **PS-1** ($44\,\mathrm{nC\,cm^{-2}}$), as demonstrated in figure 5.

4. Summary

We have synthesized two polyvinyl ether and two polysiloxane side chain polymers using vinyl ethers as the side group precursors. Both polymer types exhibit smectic phases, three representatives have ferroelectric S^*_C phases.

PVE-1 exhibits no S^*_C phase, but a broad (110°C) S_A phase which shows electroclinic switching.

Polsiloxane **PS-1**, with the same mesogenic and chiral parts as a polysiloxane **PVE-1**, exhibits a S^*_C phase from room temperature up to 170°C with a ferroelectric switching temperature range of 72°C and a P_S of $44\,\mathrm{nC\,cm^{-2}}$.

Polyvinyl ether **PVE-2** shows ferroelectric behaviour over a temperature range of 15°C and a maximum of $P_S = 32\,\mathrm{nC\,cm^{-2}}$. To our knowledge **PVE-2** seems to be the first example of a ferroelectric polyvinyl ether.

Polysiloxane **PS-2** is a ferroelectric polymer with two subphases in the S^*_C region and a high spontaneous polarization ($P_{S_{\max}} = 155\,\mathrm{nC\,cm^{-2}}$).

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