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The influence of a γ-oxygen in the spacer of liquid crystal side group polysiloxanes on their ferroelectric properties†

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Two types of side group polysiloxanes which differ in their spacer between backbone and mesogenic part were synthesized via polymer analogous reaction. The impact of an oxygen atom localized in the γ position to the siloxane main chain on the ferroelectric properties was investigated. In addition, the link between the terminal chiral moiety and the mesogenic part in each series was varied. The phase transition behaviour, spontaneous polarization and the electro-optical response time for the two series of polymers are compared. The mesophase structures were determined by X-ray measurements on magnetically oriented samples at different temperatures. The additional oxygen atom in the spacer near to the main chain leads to broader range smectic C* phases and shorter electro-optical response times, which suggests that the ether linkage promotes a better decoupling between main chain and mesogenic side group.

1. Introduction

Liquid crystalline polymers (LCPs) containing chiral moieties exhibit various electro-optical effects in their chiral mesophases analogous to those of low molecular mass ferroelectric liquid crystals (FLCs). Since 1984, LCPs with chiral smectic C* phases have been prepared and their ferroelectric properties, for example spontaneous polarization [1] and electro-optical response time, determined [2–4]. Connecting mesogenic cores via a flexible spacer to a polymer backbone generally leads to an increase of the mesophase transition temperatures, to a higher viscosity and to a shorter response time in an electric field compared to low molar mass FLCs [5]. On the other hand, a rich polymorphism occurs in side chain polymers [6–8] and some unusual behaviour, for example in electro-optic response in smectic phases, can be observed [8–11]. Therefore structural modifications and comparison of properties can help to reach an answer to the question of the potential use of liquid crystalline polymers in electro-optical devices [12, 13]. With regard to such aspects, we chose to synthesize polysiloxanes which are known to have low glass transition temperatures; they can also exhibit phase transitions at moderate temperatures, low viscosities and short switching times.

We have prepared two series of side group polysiloxanes which differ in their spacer between mesogenic unit and polysiloxane backbone. The two types of polymers are presented in scheme 1. Side group polysiloxanes (PSs) with a spacer consisting of twelve methylene units were obtained by hydrosilylation of a side group precursor with a terminal double bond, as shown in scheme 1 (*a*). In the second series the side group precursor contains a terminal vinylether group yielding polysiloxanes, PVSs (scheme 1 (*b*)), having, in addition to the twelve methylene units, one oxygen atom in the spacer in the γ position to the main chain.

Suzuki *et al.* [14] synthesized siloxane polymers containing an oxygen atom in the spacer in the δ position to the backbone. As a result of the incorporation of this oxygen, they lost the S_C^* phase in favour of an S_A phase. The first example of a chiral polysiloxane derived from a vinyl ether monomer was reported by Chiellini and Galli, but no ferroelectric properties or electro-optical investigations were described [15]. We have prepared two examples for each polymer series, which differ in their linkage of the terminal chiral moiety to the aromatic core. The mesogenic part consisting of three aromatic cores was linked with a chiral unit derived from lactic acid. The synthesized polymers PS-1, PS-2, PVS-1 and PVS-2 are shown in figure 1.

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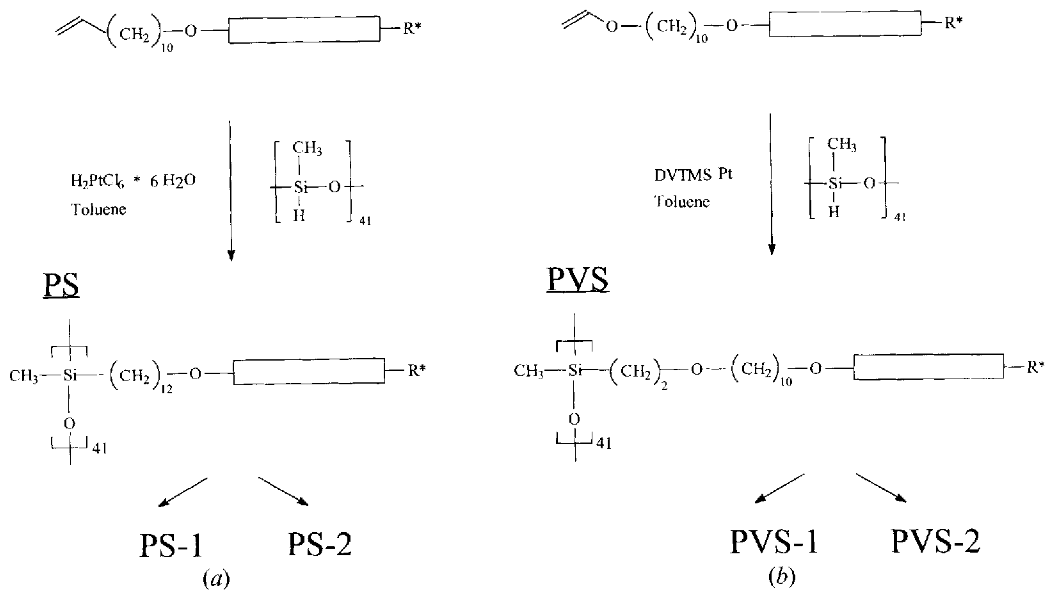


Scheme 1 (*a*). Reaction scheme for polymerization of polysiloxanes PS-1 and PS-2 derived from α-olefins.

Scheme 1 (*b*). Reaction scheme for polymerization of polysiloxanes PVS-1 and PVS-2 derived from vinyl ethers.

The influence of the ether oxygen on the one hand and the location and environment of the chiral centre on the other hand was investigated with respect to the phase transition behaviour, spontaneous polarization and electro-optical response time. X-ray investigations were carried out to characterize the mesophases of the polymers.

2. Experimental

2.1. *Synthesis*

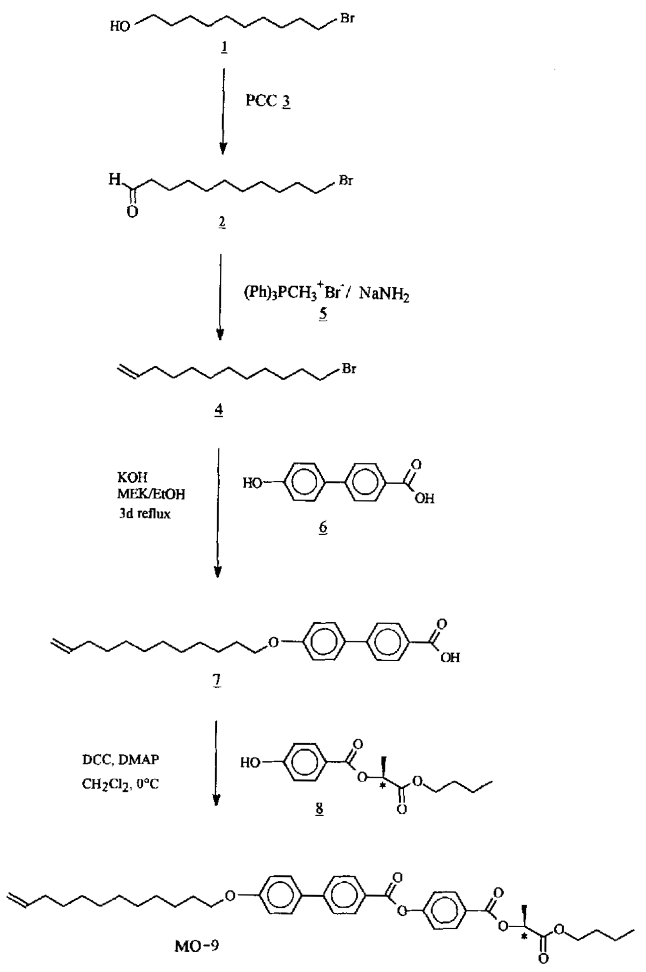
The synthesis of the mesogenic α-olefin, for simplicity named 'monomer', as precursor for PS-1 is given as an example in scheme 2. The transformation of 11-bromo-undecanol **1** to aldehyde **2** was carried out with pyridinium chlorochromate **3** (PCC) in methylene chloride [16]. Compound **4** was obtained by Wittig reaction with methyltriphenylphosphonium bromide-sodium amide mixture (Fluka) **5** in THF [17]. The etherification reaction of 12-bromo-1-dodecene **4** with 4-hydroxybiphenyl-4′-carboxylic acid **6** gave 4-(12-dodecenoyloxy)-biphenyl-4′-carboxylic acid **7**. The chiral phenolic ester **8** was synthesized by coupling *S*-butyl lactate with 4-benzyloxybenzoic acid under standard Steglich conditions and subsequent deprotection by hydrogenolysis using palladium on activated carbon. The mesogenic α-olefin MO-9 was prepared by esterification of **7** with compound **8** [18]. The target monomer was purified by silica gel column chromatography and by recrystallization from diethyl ether/acetone.

The monomer MO-10 (see figure 2) was synthesized in an analogous manner, except that the lactic acid was attached to the phenol via a Mitsunobu reaction.

Monomer MO-9, *(S)-(-)-4-[1-(butoxycarbonyl)-ethoxycarbonyl]phenyl 4′-(11-dodecenyloxy)biphenyl-4′carboxylate.* ^{1}H NMR: δ=0·92 (t, J=7 Hz, 3H); 1·24–1·70 (m, 18H); 1·64 (d; J=7 Hz, 3H); 1·82 (quint, J=7 Hz, 2H); 2·04 (dt, J=7 Hz, 2H); 4·01 (t, J=7 Hz, 2H); 4·18; 4·20 (ABt, J=13 and 6·5 Hz, 2H); 4·93 (ddt, J=10; 1·5 and 1 Hz, 1H); 4·99 (ddt, J=17; 1·5 and 1·5 Hz, 1H); 5·33 (q, J=7 Hz, 1H); 5·82 (ddt, J=17; 10 and 7 Hz, 1H); 7·00; 7·60 (AA′BB′, J=8·5 Hz, 4H); 7·34; 8·23 (AA′BB′, J=8·5 Hz, 4H); 7·70; 8·18 (AA′BB′, J=8·5 Hz, 4H). MS: *m*/*e*= calculated 628, 8012; found 628, 3400 (HR, 10 per cent M^+, $C_{39}H_{48}O_7$); 363 (100 per cent, M-$C_{14}H_{17}O_5$), 196 (3 per cent, $C_{13}H_8O_2$). $[\alpha]_D^{25}=-13{\cdot}2°$ ($CHCl_3$, c=0·6).

Monomer MO-10, *(S)-(-)-4-[1-(butoxycarbonyl)-ethoxy]phenyl 4′-(11-dodecenyloxy)biphenyl-4′-carboxylate.* ^{1}H NMR: δ=0·91 (t, J=7 Hz, 3H); 1·25–1·66 (m, 18H); 1·63 (d, J=7 Hz, 3H); 1·81 (quint, J=7 Hz, 2H); 2·04 (dt, J=7 Hz, 2H); 4·01 (t, J=7 Hz, 2H); 4·16; 4·18 (ABt, J=13 and 6·5 Hz, 2H); 4·74 (q, J=7 Hz, 1H); 4·93 (ddt, J=10; 1·5 and 1 Hz, 1H); 4·99 (ddt, J=17; 1·5 and 1·5 Hz, 1H); 5·82 (ddt, J=17; 10 and 7 Hz, 1H); 6·92; 7·13 (AA′BB′, J=9 Hz, 4H); 7·00; 7·59 (AA′BB′, J=9 Hz, 4H); 7·68; 8·21 (AA′BB′, J=9 Hz, 4H). MS: *m*/*e*= calculated 600,7912; found 600,3451 (HR, 10 per cent, M+, $C_{38}H_{48}O_6$); 363 (100 per cent, M-$C_{13}H_{17}O_4$); 196 (3 per cent, $C_{13}H_8O_2$). $[\alpha]_D^{25}=-15{\cdot}4°$ ($CHCl_3$, c=1·0).

The syntheses of the mesogenic vinyl ether monomers MO-11 and MO-12 were described in a previous paper [19]. The polysiloxanes PS-1 and PS-2 were obtained by hydrosilylation with poly(hydrogenmethylsiloxane)



Scheme 2. Synthesis route for monomer MO-9.

(P*n* = 41) of the mesogenic α-olefins MO-9 and MO-10 in toluene in the presence of hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) [20]. After precipitation from methanol three times and drying under vacuum, pure polymers were obtained in 29–34 per cent yield. The other series of polysiloxanes, PVS-1 and PVS-2, was also prepared by hydrosilylation using the H-siloxane (P*n* = 41) and the vinyl ether monomers MO-11 and MO-12. The catalyst used above does not work in this case. For that reason we used platinum divinyltetramethyldisiloxane (DVTMS) [15]; see scheme 1(*b*). PVS-1 and PVS-2 were obtained as white–grey solids (yield: 50–60 per cent).

2.2. *Measurements*

The characterization of each compound synthesized was effected by ^1H 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

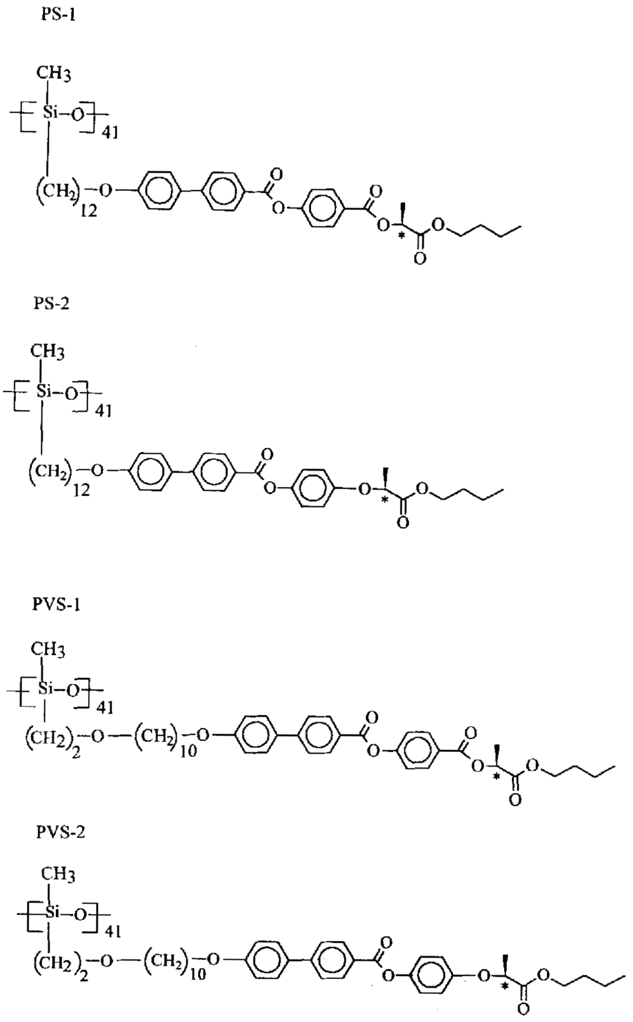


Figure 1. Molecular structures of polysiloxanes.

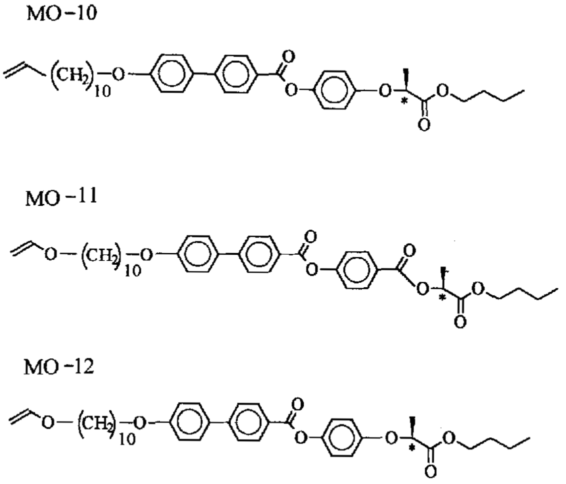


Figure 2. Molecular structures of monomers MO-10, MO-11 and MO-12.

scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 at a scanning rate of $5\,\mathrm{K\,min^{-1}}$ and the phases were identified using polarizing optical microscopy and 4–10 μm thick polyimide coated cells.

The spontaneous polarization was measured by the triangular wave method [21]. The switching time was measured as the time of change of transmitted light intensity from 10 per cent to 90 per cent with crossed polarizers and applying a rectangular wave voltage.

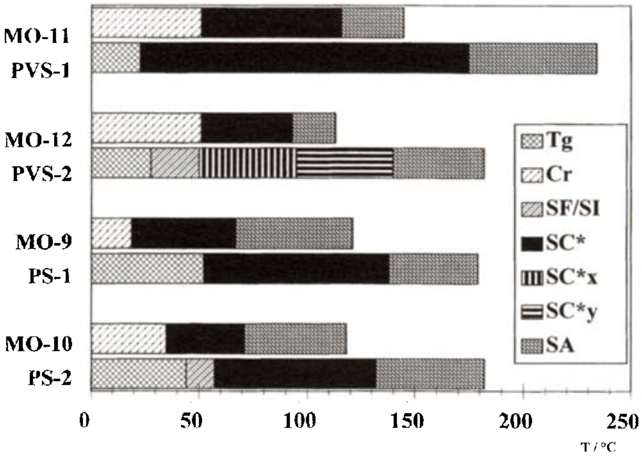


Figure 3. Phase transition temperatures of monomers and polymers.

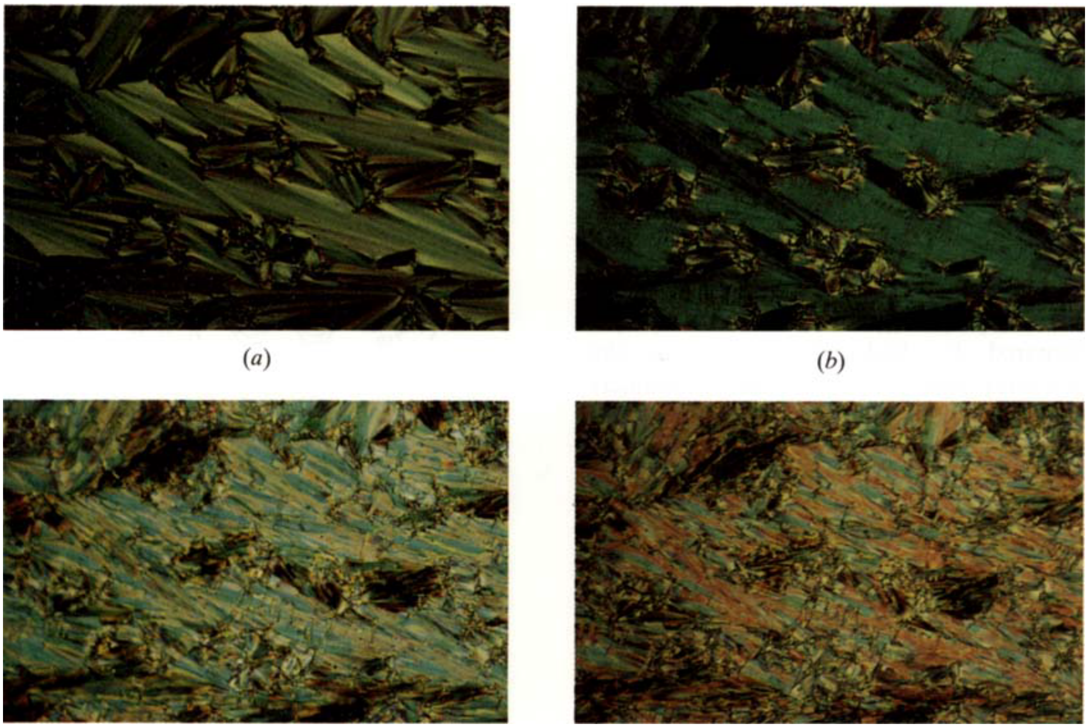
X-ray diffraction measurements were carried out in a custom made temperature controlled ($\Delta T = \pm 0{\cdot}1\,\mathrm{K}$) vacuum chamber with a flat film camera at a distance of 81 mm from the sample. Monochromatic CuK_α radiation ($\lambda = 0{\cdot}15418\,\mathrm{nm}$, graphite monochromator) was focused by a glass capillary. The polymer sample was oriented inside the chamber in a magnetic field (2·4 T) perpendicular to the incident beam.

3. Results and discussion

3.1. *Phase behaviour and molecular weights*

The phase transition temperatures for the monomers and polymers are shown in figure 3. All polymers and monomers exhibit enantiotropic $\mathrm{S_C^*}$ and $\mathrm{S_A}$ phases. For all polymers, the $\mathrm{S_C^*}$ region is much broader than for their respective monomers. On slowly cooling from the isotropic phase into the liquid crystalline phase, typical fan-shaped textures of an $\mathrm{S_A}$ phase were observed for all polymers. The $\mathrm{S_C^*}$ phases appeared as broken fan-shaped textures.

For the PS-series, the phase transition temperatures are higher than those of their corresponding monomers MO-9 and MO-10 whereas, for the polymers PVS-1 and PVS-2, the $\mathrm{S_C^*}$ mesophase ranges start at lower temperatures compared to their monomers. PVS-1 exhibits a smectic C* phase from room temperature up to 175°C. PS-2 and PVS-2, which have the same molecular struc-



(*a*) (*b*)

(*c*) (*d*)

Figure 4 (*a*–*d*) Optical photomicrographs of the (*a*) $\mathrm{S_A}$ (125°C), (*b*) $\mathrm{S_{CY}^*}$ (160°C), (*c*) $\mathrm{S_{CX}^*}$ (90°C), (*d*) $\mathrm{S_F/S_I}$ (18°C) textures of PVS-2 ture except for the spacer, show a second tilted phase (S_F/S_I) below the S_C^* phase. This phase does not occur in the case of PS-1 and PVS-1. Therefore the chiral moiety (lactic-phenyl ether) is responsible for the S_F/S_I phase formation.

As reported recently [19], the polysiloxane PVS-2 exhibits two smectic subphases $S_{C_X}^*$ and $S_{C_Y}^*$. These two subphases show different textures by polarizing microscopy. The textures for the S_A, $S_{C_Y}^*$, $S_{C_X}^*$ and S_F/S_I phases in PVS-2 are presented in figure 4(*a–d*). The $S_{C_Y}^*$–$S_{C_X}^*$ phase transition could also be detected by DSC for the polysiloxane PVS-2. A step at 95°C in the DSC curve indicates the phase transition from $S_{C_Y}^*$ to $S_{C_X}^*$ phase. Below the $S_{C_X}^*$ phase, a higher ordered smectic phase (S_F/S_I) was detected by DSC (see figure 5) and confirmed by X-ray measurements (see §3.3.). The molecular weights (M_W) of the polymers synthesized are shown in table 1. The M_W values for PS-1 and PS-2 are higher than for PVS-1 and PVS-2, which were prepared first. These differences in molecular weights we attribute to an ageing process of our poly(hydrogenmethylsiloxane) PHMS sample.

3.2. *Ferroelectric properties*

The temperature dependence of the switching time of polysiloxanes PS-1, PS-2, PVS-1 and PVS-2 is shown in figure 6 as a function of reduced temperature T_{red}. The measurements were carried out at relatively low voltage

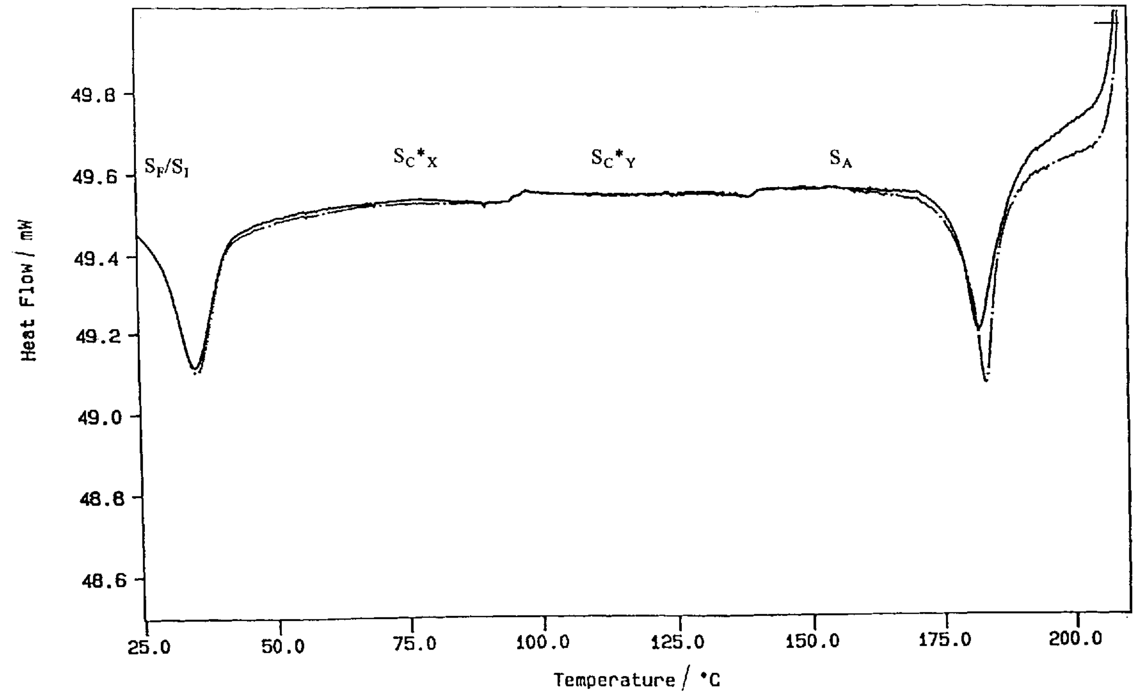


Figure 5. DSC traces of PVS-2 (1st and 2nd cooling curves).

Table 1. Phase transition temperatures, molecular weights and spontaneous polarizations of monomers and polymers.

Monomers/polymers	Phase transition temperature/°C	Molecular weight M_w/g mol^{-1}	M_w/M_n	Ps (max)/nC cm^{-2}	[a]Ps*/nC cm^{-2}
MO-9	Cr 19 S_C^* 67 S_A 121 I	628		75	19
PS-1	Tg 52 S_C^* 138 S_A 179 I	24000	2·17	57	
MO-10	Cr 35 S_C^* 71 S_A 118 I	600		139	43
PS-2	Tg 44 S_F/S_I 57 S_C^* 132 S_A 182 I	29000	2·17	89	
MO-11	Cr 51 S_C^* 116 S_A 145 I	644		94	38
PVS-1	Tg 23 S_C^* 175 S_A 234 I	22400	1·7	44	
MO-12	Cr 51 S_C^* 93 S_A 113 I	616		132	71
PVS-2	S_F/S_I 28 $S_{C_X}^*$ 95 $S_{C_Y}^*$ 140 S_A 182 I	21500	1·7	155	

[a] Ps* measured 20°C below the S_A–S_C^* transition temperature.

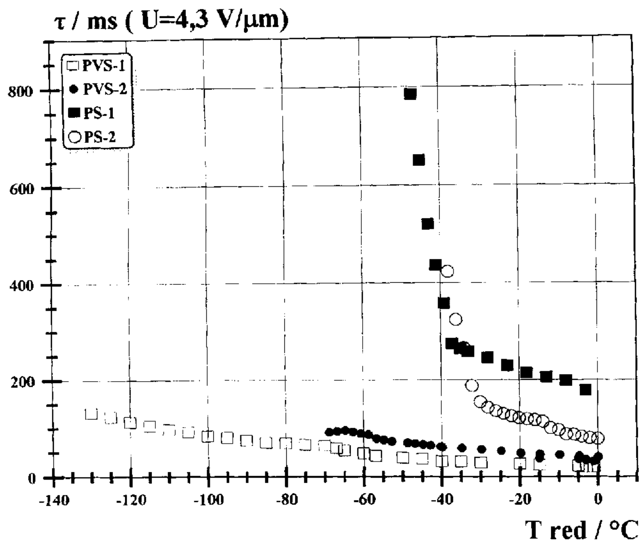


Figure 6. Temperature dependence of switching time of polysiloxanes PS-1, PS-2, PVS-2 and PVS-2.

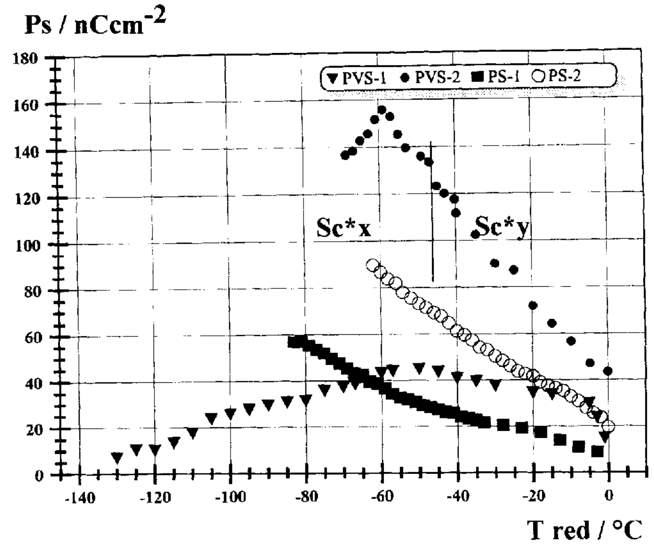


Figure 7. Temperature dependence of spontaneous polarization of polysiloxanes PS-1, PS-2, PVS-2 and PVS-2.

($U = 4{\cdot}3\,\mathrm{V\,\mu m^{-1}}$). The polysiloxanes PVS-1 and PVS-2 prepared from vinyl ethers show a distinctly faster switching compared to PS-1 and PS-2. Consequently, this suggests an improved decoupling between the main chain and the mesogenic groups caused by the additional ether linkage, which increases the mobility of the mesogenic side groups. This phenomenon was also observed recently for a ferroelectric liquid crystalline polyoxyethylene with an ether oxygen in the spacer in the β position to the backbone [22]. Inclusion of further oxygen units in the spacer caused an increase in the response time.

The spontaneous polarizations of the two series of polymers are shown in figure 7. The polymers PVS-2 and PS-2, which have an ether linkage between the chiral moiety and the aromatic core, exhibit the highest values of spontaneous polarization (PVS-2: $155\,\mathrm{nC\,cm^{-2}}$ and PS-2: $89\,\mathrm{nC\,cm^{-2}}$). This effect is plausible, since the chiral centre is more closely linked to the rigid core. On the other hand it leads to a narrower range S_C^* phase and to the occurrence of an S_F/S_I phase. The unusual drop in the spontaneous polarization of PVS-2 can be explained by the increase of the viscosity with decreasing temperature and has also been observed in other cases [2, 23]. The values of the spontaneous polarization for the polymers and monomers are shown in table 1.

3.3. *X-ray investigations*

For a detailed study of the influence of the ether bridge in the spacer on the type of mesophases and the ferroelectric behaviour, we selected polymers PS-2 and PVS-2 . The mesophase assignment was determined by X-ray diffraction measurements on magnetically oriented samples at different temperatures. PVS-2 shows two smectic C* phases $S_{C_X}^*$ and $S_{C_Y}^*$ which have been previously described [19]. In table 2, the layer periodicities, the mean lateral mesogen distances and the half width values of the wide angle crescent (FWHM) are presented.

The main difference between the two polymers is that for PVS-2 in the smectic C* region two sub-phases $S_{C_X}^*$

Table 2. X-ray diffraction data for PS-2 and PVS-2.

Polymer	Phase	Temperature T/°C	Layer periodicity d/nm	Lateral mesogen distance D/nm	FWHM $\Delta\,(2\Theta)$/°
PVS-2	S_A	160	3·8	0·474	
	$S_{C_Y}^*$	121	3·71	0·461	3·9
	$S_{C_X}^*$	75	3·6	0·456	3·0
	S_F/S_I	18	3·75	0·446	1·8
PS-2	S_A	175	3·82	0·479	5·8
	S_C^*	100	3·71	0·459	4·5
	S_F/S_I	23	3·86	0·445	2·7

and $S_{C_Y}^*$ exist. The X-ray investigations in the region of these two phases show a difference in the layer periodicity and a decrease of the half width of the wide angle crescents, which correspond to smaller variations of the lateral separation of the mesogenic units. For PS-2 there is no evidence for the occurrence of two sub-phases in the smectic C* region. We found for the S_C^* phase a layer periodicity and lateral mesogen distance which are comparable with the values for the $S_{C_Y}^*$ phase for PVS-2 (see table 2). In addition to the S_C^* phases for both polymers, we observed a S_F/S_I phase below the smectic C* phases. The phase transition S_C^* to S_F/S_I is connected with a remarkable decrease of the half width of the wide angle crescents (see table 2).

4. Summary

Two types of ferroelectric liquid crystalline polysiloxanes were synthesized. One type was prepared by a conventional hydrosilylation reaction of α-olefins. The other type was obtained by the same reaction with mesogenic vinyl ethers which leads to an oxygen atom in the spacer.

The influence of the spacer oxygen in the γ position to the polysiloxane backbone on the ferroelectric and mesomorphic behaviour was investigated. The two polymers PVS-1 and PVS-2 with the oxygen bridge in the spacer show broader range smectic C* phases. The ether oxygen in the spacer improves the mobility of the mesogenic side groups. The switching for PVS-1 and PVS-2 is about one order of magnitude faster than for PS-1 and PS-2. The origin of the rich polymorphism (occurrence of three tilted phases) for PVS-2 may be caused by the combined effects of the ether oxygen in the spacer and in the tail group with the centre of chirality close to the core.

Due to the enlarged S_C^* phase range PVS-2 exhibits a higher spontaneous polarization than the monomer. The polysiloxanes PS-2 and PVS-2 have spontaneous polarizations of $89\,\mathrm{nC\,cm^{-2}}$ and $155\,\mathrm{nC\,cm^{-2}}$, respectively, due to the closer link of the chiral moiety to the aromatic core. They show S_F/S_I phases below the smectic C* phases.

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References

[1] Shibaev, V. P., Kozlovsky, M. V., Beresenev, L. A., Blinov, L. M., and Plate, N. A., 1984, *Polym. Bull.*, **12,** 299.

[2] Uchida, S., Morita, K., Miyoshi, K., Hashimoto, K., and Kawasaki, K., 1988, *Mol. Cryst. Liq. Cryst.*, **155,** 93.

[3] Scherowsky, G., Schliwa, A., Springer, J., Kühnpast, K., and Trapp, W., 1989, *Liq. Cryst.*, **5,** 1281.

[4] Kapitza, H., Zentel, R., Twieg, R. J., Nguyen, C., Vallerien, S., Kremer, F., and Willson, C. G., 1990, *Adv. Mater.*, **2,** 539.

[5] Scherowsky, G., 1995, *Ferroelectric Polymers*, edited by H. S. Nalwa (New York: Marcel Dekker Inc.).

[6] Poths, H., and Zentel, R., 1994, *Liq. Cryst.*, **16,** 749.

[7] Davidson, P., and Levelut, A. M., 1992, *Liq. Cryst.*, **11,** 469.

[8] Davidson, P., Kühnpast, K., Springer, J., and Scherowsky, G., 1992, *Makromol. Chem.*, **193,** 3097.

[9] Scherowsky, G., Kühnpast, K., and Springer, J., 1991, *Makromol. Chem. rap. Commun.*, **12,** 381.

[10] Bömmelburg, J., Heppke, G., and Hollidt, J., 1991, *Makromol. Chem. rap. Commun.*, **12,** 483.

[11] Skarp, K., Andersson, G., Gouda, F., Lagerwall, S. T., Poths, H., and Zentel, R., 1992, *Polym. adv. Technol.*, **3,** 241.

[12] Kiefer, R., 1995, *Ferroelectric Polymers*, edited by H. S. Nalwa (New York: Marcel Dekker Inc.).

[13] Komitov, L., Lagerwall, S. T., Stebler, B., Chiellini, E., Galli, G., and Strigazzi, A., 1993, *Modern Topics in Liquid Crystals*, edited by A. Buka (World Scientific), p. 301.

[14] Suzuki, T., and Okawa, T., 1988, *Makromol. Chem. rap. Commun.*, **9,** 755.

[15] Chiellini, E., Galli, G., Dossi, E., Cioni, F., and Gallot, B., 1993, *Macromolecules*, **26,** 849.

[16] Tietze, L. F., and Eicher, T., 1991, *Reaction and Synthesis*, (Stuttgart: Georg Thieme Verlag), p. 97.

[17] Schlosser, M., and Schaub, B., 1982, *Chimia*, **36,** 396.

[18] Neises, B., and Steglich, W., 1978, *Angew. Chem.*, **90,** 7.

[19] Scherowsky, G., Fichna, U., and Wolff, D., 1995, *Liq. Cryst.* **19,** 621.

[20] Gray, G. W., Lacey, D., Nestor, G., and White, M. S., 1986, *Makromol. Chem. rap. Commun.*, **7,** 71.

[21] Miyasato K., Abe S., Takezoe H., Fukuda A., and Kuze E., 1983, *Jpn. J. appl. Phys.*, **22,** 661.

[22] Kawasaki, K., Moriwaki, F., Hachiya, S., Endo, H., Sekiya, T., and Hashimoto, K., 1993, *Ferroelectrics*, **148,** 245.

[23] Kühnpast, K., Diss., 1993, TU Berlin.