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Fast switching ferroelectric liquid-crystalline polymers

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Ferroelectric liquid-crystalline side chain polymers containing polyacrylate or polysiloxane main chains, a mesogenic unit of three aromatic cores and chiral end groups were synthesized and characterized by D.S.C., optical microscopy, and X-ray diffraction. Polyacrylates with a flexible spacer of eleven methylene groups exhibit fast bistable switching in oriented samples (2 to 4 μm cells) with response times of some ms at low D.C. voltages, making these polymers interesting for the fabrication of electrooptical devices. Somewhat longer response times were found for the first switchable polysiloxanes. In this case some problems in obtaining well orientated samples have to be solved.

1. Introduction

Ferroelectricity in liquid crystals has gained considerable attention in the last few years in both basic research and potential technological applications. The development of bistable fast switching displays exhibiting response times in the range of some μs has created considerable interest in the synthesis and investigation of new ferroelectric materials with high spontaneous polarization. The extraordinary properties found in low molar mass ferroelectric liquid crystals posed the question, as to whether liquid crystalline polymers exhibiting chiral smectic C* phases may also show short switching times. The switching times of *nematic liquid-crystalline polymers* due to their high viscosity are known to be in the range of seconds, that means two to three orders of magnitude higher compared with low molecular weight liquid crystals. For this reason, the applicability of polymers in high performance fast switching devices seemed to be less promising.

Are shorter switching times to be expected in *ferroelectric liquid-crystalline polymers* because the orientational change of the mesogenic side group in the S_C^* phase requires only motion on a cone over the double tilt angle? The aim of this work was to find an answer to this question: There are few reports on liquid-crystalline polymers exhibiting chiral smectic C phases [1–10]. Ferroelectric properties, e.g. spontaneous polarization in these polymers, have been established in two types of substances [1, 5, 6, 9]. In one case switching times have been reported [9]. To succeed in the synthesis of ferroelectric liquid-crystalline polymers we choose two approaches.

(1) We have selected a polymer having a broad smectic C phase and we have introduced chirality at appropriate positions within the molecule. By introducing a chiral branching into the spacer unit we have obtained polymers with a chiral smectic phase [10]. In these systems no switching properties could be observed as yet.

(2) We have synthesized liquid crystal monomers exhibiting broad S_C^* phases and a high spontaneous polarization hoping to transfer this quality to the polymer. Polyacrylate and polysiloxane were used as the main chain.

2. General part

2.1. *Ferroelectric polyacrylates*

The polymers **14** and **15**, having 2-octylether and **16** with 2-chloro-3-methylpentanoate as the chiral unit were synthesized in seven steps as follows (see scheme 1).

Methyl ω-alkenyloxybenzoate **2**, obtained by etherification of methyl 4-hydroxybenzoate with undec-10-en-1-yl tosylate (**1**) was saponified and combined with monosilylated 4,4′-dihydroxy-biphenyl to give **4** (after deprotection). Etherification of **4** with *S*-(-)-octan-2-ol using the Mitsonubo reaction [dimethyl azodicarboxylate (DEAD) plus triphenylphosphine (TPP)] yielded **5**, which exhibited six mesophases including a broad S_C^* phase, and two blue phases. Hydroxylation using diborane resulted in **6**, which reacted with acryloylchloride to give the monomer **7**. The polymerization was performed in THF with 1 mol % of AIBN as initiator (8 h, 60°C) to give the polymer **14**.

Polymers **15** and **16** were obtained in the following reaction sequence (see scheme 2). ω-Hydroxy-alkyloxybenzoic acids **8** and **9**, obtained by etherification of 4-hydroxybenzoic acid with ω-bromoalkan-1-ols, were transformed into the acrylates **10** and **11** in analogy to the pathway in scheme 1. Thereafter, the chiral endgroups were introduced to give the monomers **12** and **13**. **12** exhibits six mesophases including a S_C^*, and two blue phases (see table 1). Polymerization of **12** and **13**, performed as described for **7**, yielded **15** and **16**.

2.2. *Properties of the polyacrylates* **14–16**

For polymer **14** an average molecular weight M_w of λ 210 000 was determined by G.P.C. (polystyrene calibration). D.T.A. measurements reveal four mesophases (see figure 1).

Above the glass transition at ~ 50°C a higher ordered orthogonal smectic phase occurs, the X-ray diffraction pattern of which shows a sharp wide angle reflection (see figure 2). The X-ray photograph was taken from a fibre drawn at ~ 135°C (in the S_C^* phase), and thereafter annealed for 20 min at 70–80°C. The layer spacing of 43·6 Å is

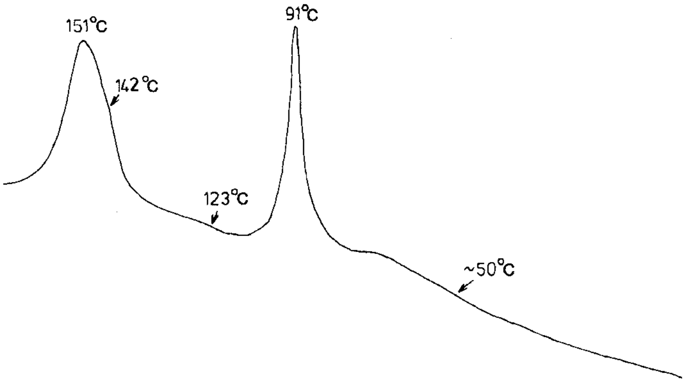
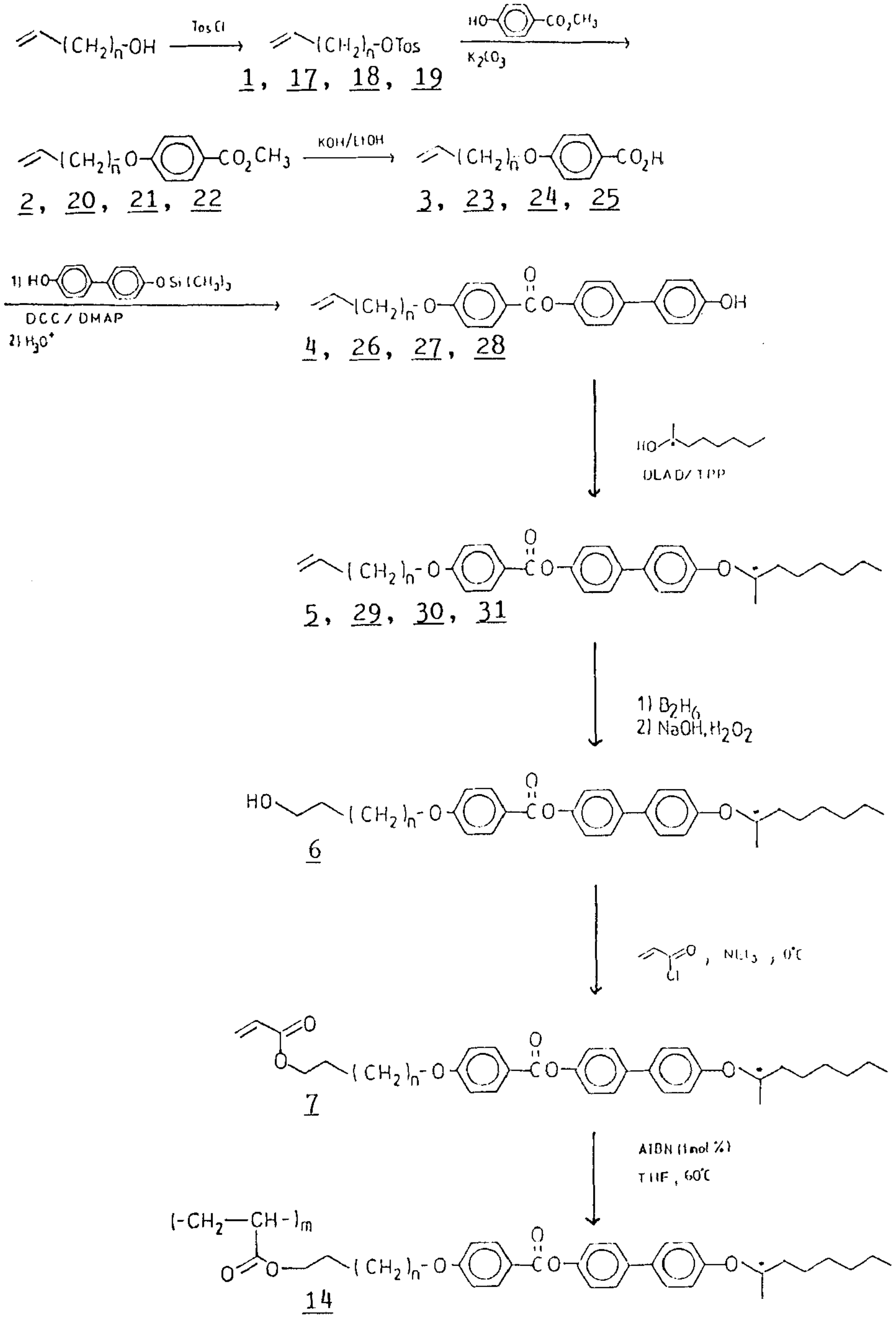
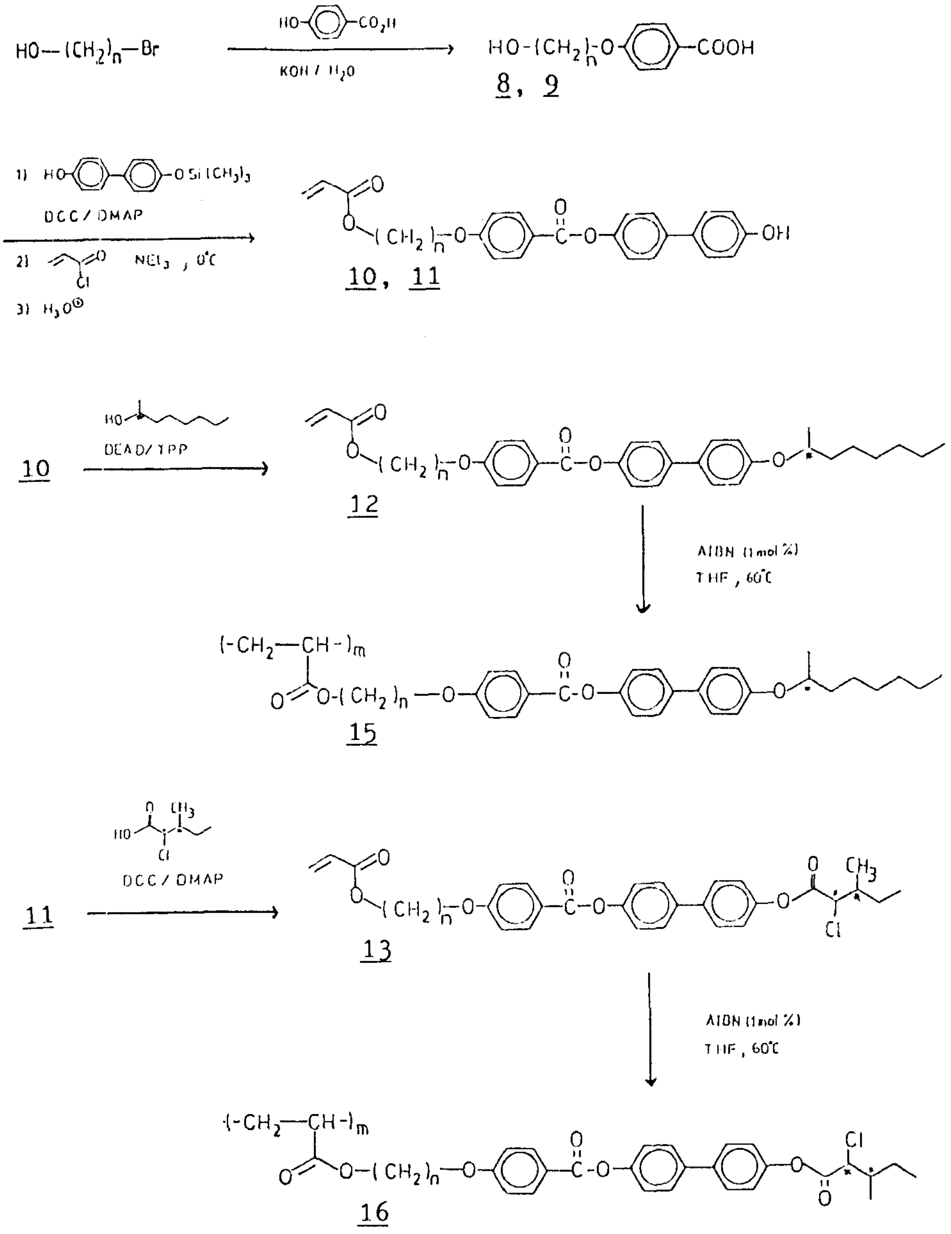


Figure 1. D.T.A. measurement of polymer **14** heating curve, 10 K/min.



n								
9	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**14**
8	**17**	**20**	**23**	**26**	**29**			
6	**18**	**21**	**24**	**27**	**30**			
4	**19**	**22**	**25**	**28**	**31**			

Scheme 1.



n				
10	**8**	**10**	**13**	**16**
8	**9**	**11**	**12**	**15**

Scheme 2

in agreement with the calculated length of the side group (43 Å, taken from a space filling model; see table 2). An orthogonal smectic phase can therefore be assumed. Above the transition temperature of 92°C a tilted smectic phase is formed, which transforms at 128°C into another smectic phase (S_C^*) (see table 1) having the same tilt angle of 34°, deduced from the layer spacing (see table 2). At 142°C a third phase

Table 1. Transition temperatures (in °C) of monomers (**M**) and the corresponding polyacrylates (**P**).

No.										Switcable
M **5**	C 63·2	S_X 69·1			S_C^* 100·2	S_A 107·6	N* 115·0	BP_I 116·4	BP_{II} 116·5 I	+
M **6**	C 74·2				S_C^* 91·2	S_A 103·7	N* 119·3	BP_I 121·1		+
M **7**	C 57·1	S_X 62·2			S_C^* 75·4	S_A 92·3	N* 93·3	BP_I 95·3	BP_{II} 95·4 I	+
P **14**	T_G 50	S_1 92	S_2 128		S_C^* 143	S_4 151 I				+
M **12**	C 55·2				S_C^* 75·8	S_A 82·3	N* 100·6	BP_I 105·9 I		+
P **15**	T_G 80	S167 I								−
M **13**	polymerizes by heating									−
P **16**	T_G-20	S_1 60	S_2 105	S_3 164 I						+

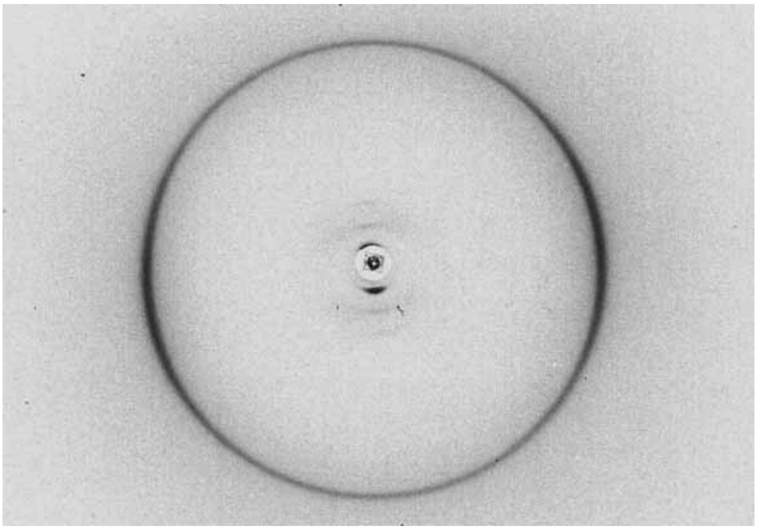


Figure 2. Fibre X-ray pattern of polymer **14** at room temperature. Fibre drawn at 135°C and annealed at 80°C, fibre axis vertical.

Table 2. Temperature dependent X-ray measurement of polymer **14**.

T/°C	d_{sl}/nm	d_l/nm	tilt angle/°
75	4·36	0·44	0
100	3·57	0·46	34
129	3·57		34
138	3·57		34
145	3·72		30
149·5	3·8		28

Length of the side chain: 4·3 nm. d_{sl}: smectic layer spacing. d_l: lateral spacing of the mesogens.

transition occurs. Above this temperature the layer spacing decrease (see table 2). The four phase transitions are clearly observable by optical microscopy. The textures of the three smectic phases between 50°C and 142°C are displayed in figure 3; all three show (in part) schlieren textures. In the areas of the fan textures at the transition of 124°C a transformation to broken fans takes place; this is typical for S_C^* phases.

2.3. *Switching properties*

In the temperature range 118–142°C oriented samples of polymer **5** exhibit fast switching at low D.C. voltages. The temperature dependence of the response time is shown in figure 4. In a 2 μm cell, driven by a square voltage of 40 V, response times between 1 and 2·7 ms were measured. Apart from this fast switching process another exciting phenomenon is the shorter response time found in the higher ordered phase below 126°C. At the phase transition from this S_X to the S_C^* phase the response time increases significantly. With further increase of temperature the response time again falls because of the decreasing viscosity in the polymer.

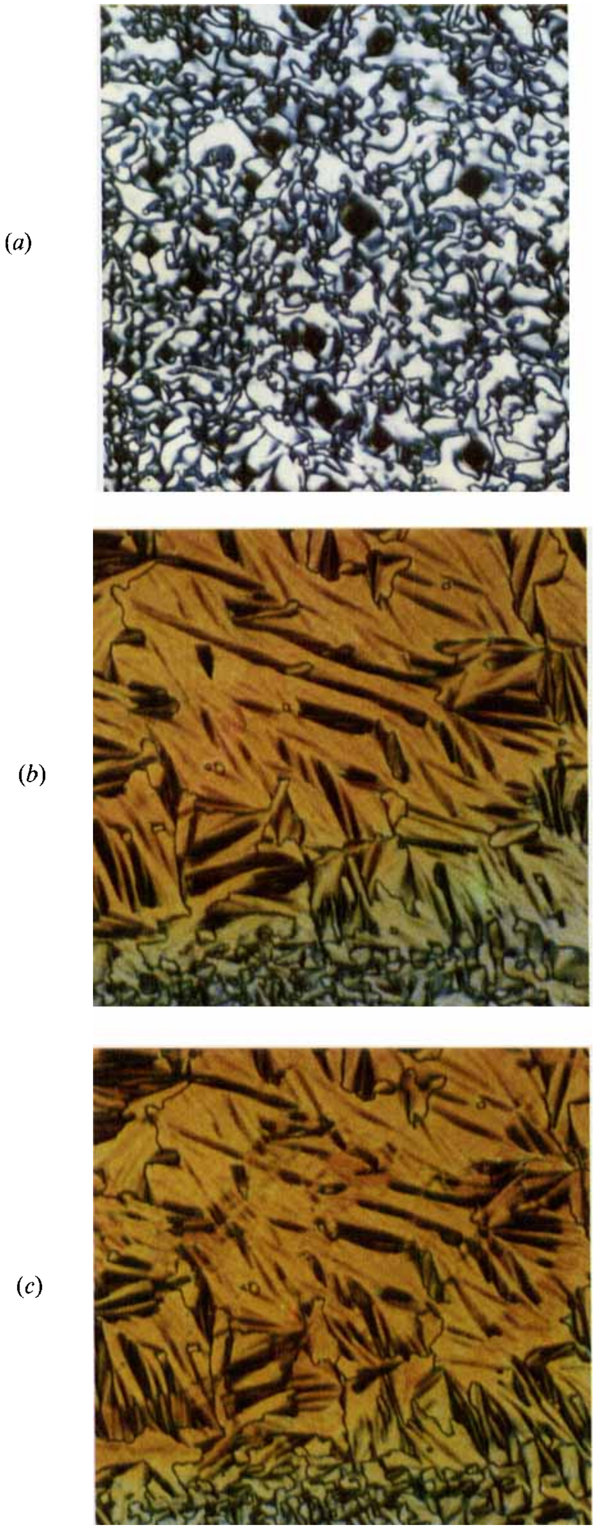


Figure 3. Textures of polymer **14**; (*a*) S_1, (*b*) S_2, and S_C^* phase.

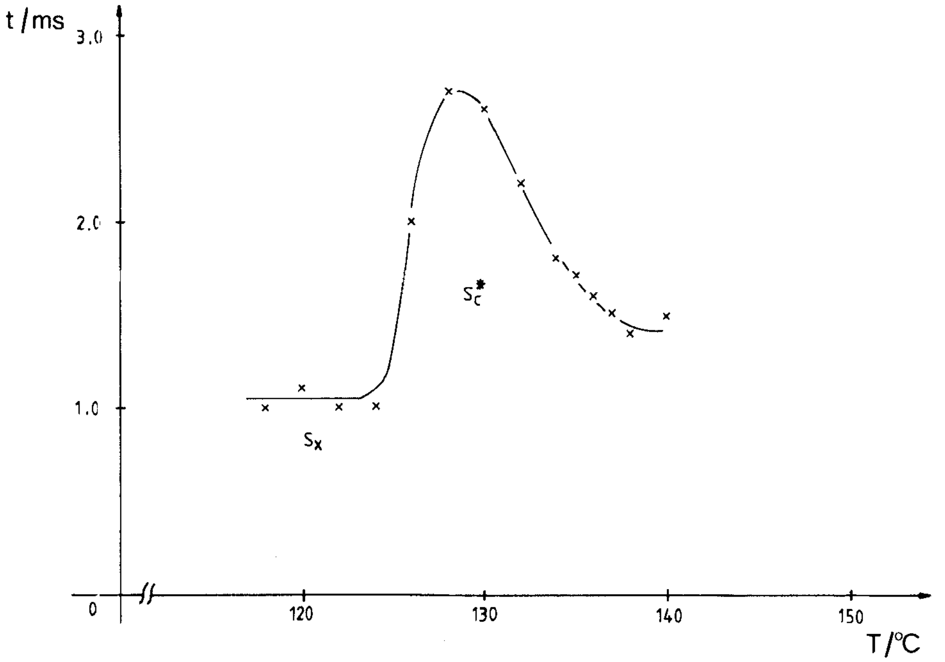


Figure 4. Temperature dependence of the response time of polymer **14** at 40 V, 2 µm cell.

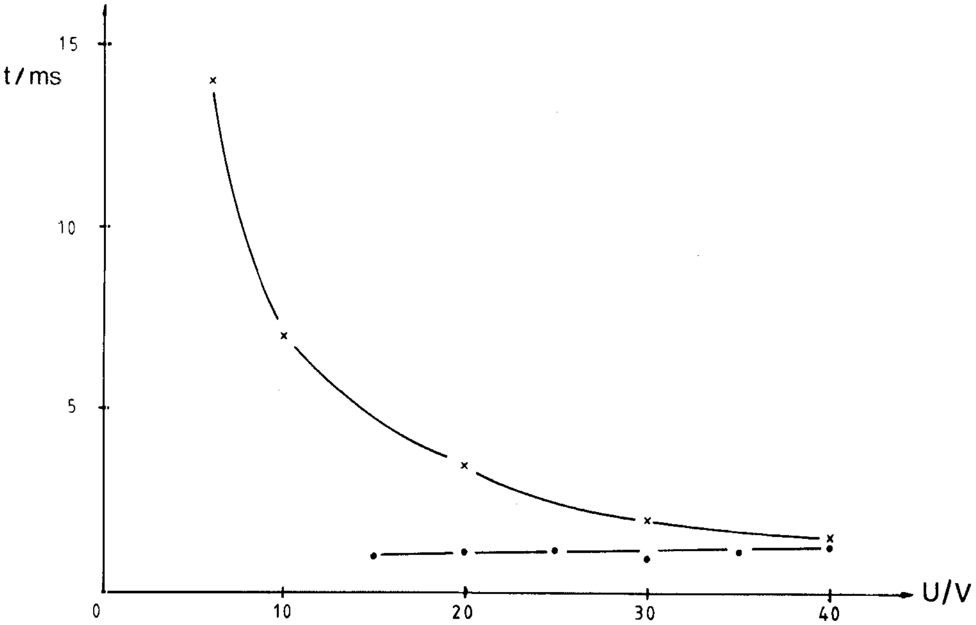


Figure 5. Response time versus applied D.C. voltage for polymer **14** at 125°C (●) and 137°C (x).

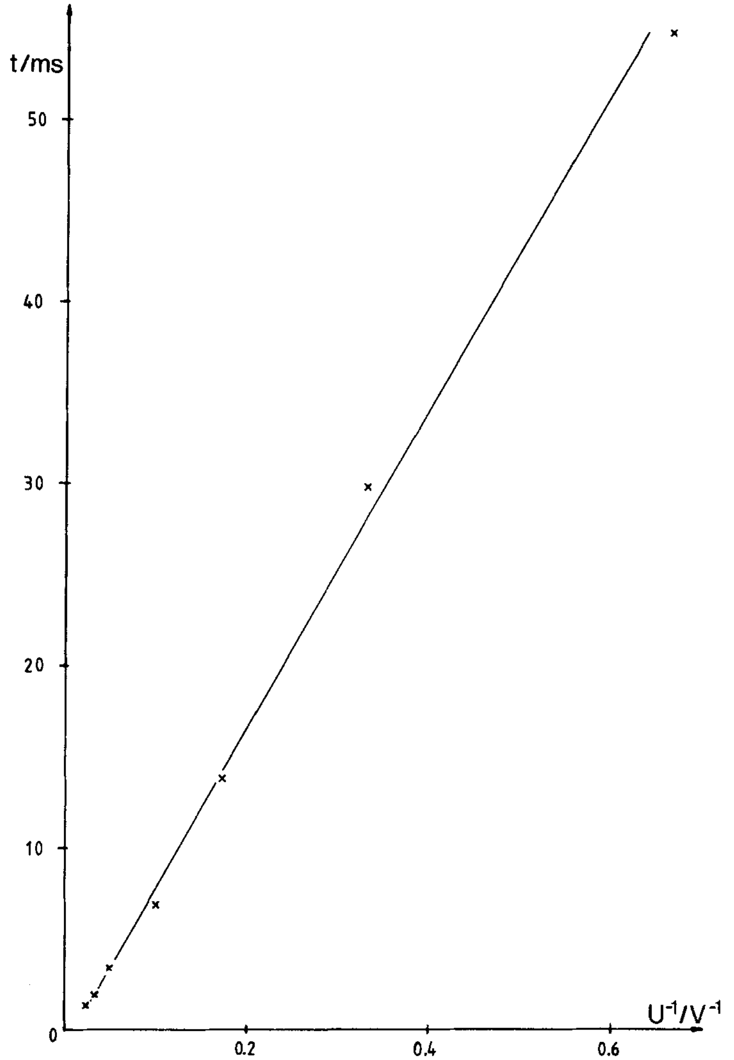


Figure 6. Response time versus reciprocal voltage.

There is a distinct difference between the switching processes in the two smectic phases. Whereas the true ferroelectric switching in the S_C^* phase takes place between two stable states, this does not hold for the higher ordered S_X phase. In this case, an electroclinic effect is operating. This effect is known for S_A phases formed from chiral molecules having high spontaneous polarization. In contrast to ferroelectric switching, the electroclinic effect has no bistability. The electric field causes a tilt of the orthogonally arranged molecules in the smectic layer; the tilt angle depends on the applied voltage. The electroclinic effect can be distinguished from bistable ferroelectric switching by measuring the dependence of the response time upon the applied sine wave voltage. Whereas in the S_C^* phase switching is observed between two stable states shortly after the field changes sign, in the higher ordered S_X phase the transmission changes continuously with the applied field. A further indication can be drawn from response time measurements with different field strengths.

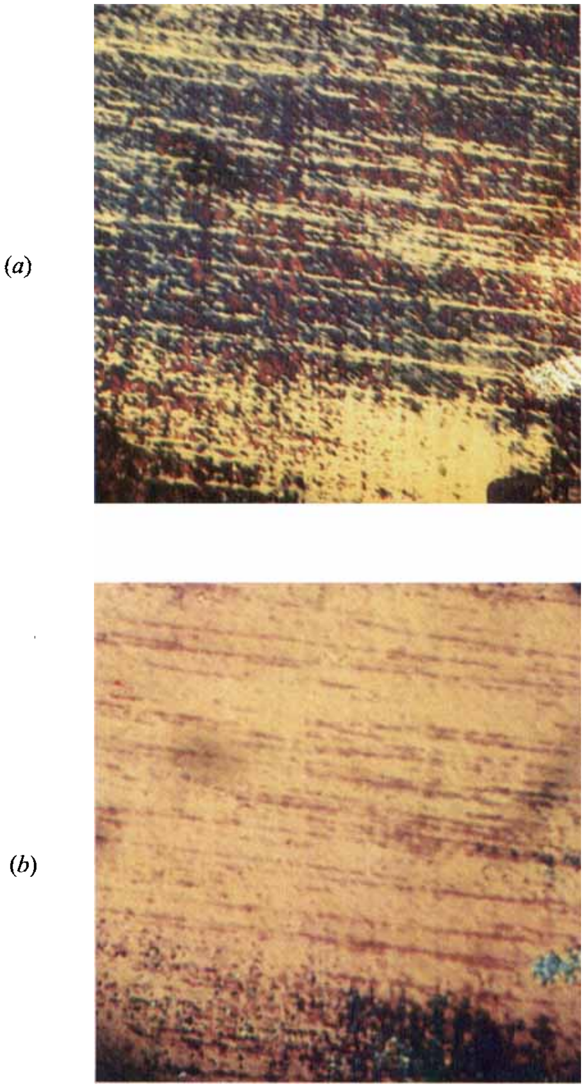


Figure 7. The two stable switching states of polymer **14** in a 4 μm cell at 137°C.

In figure 5 the response time is plotted versus the applied voltage for two temperatures. At 125°C the response time is almost independent of the applied field, in accord with the electroclinic effect. At 137°C in the S_C^* phase the response time decreases distinctly with increasing voltage. A plot of the response time versus reciprocal voltage is shown in figure 6; it shows an almost linear dependence. This is further proof of the ferroelectric switching process. At present, there is an open question as to why the higher ordered tilted smectic phase shows an electroclinic behaviour instead of ferroelectric switching. Presumably the viscosity in this phase prevents the mesogens from reaching the other stable state. The late beginning of the measurable response only at 118°C in this phase which exists from 91°C is probably also caused by the high viscosity. Figure 7 shows the two stable switching states in a 4 μm cell at 137°C. Further investigations are in progress to understand the observed properties.

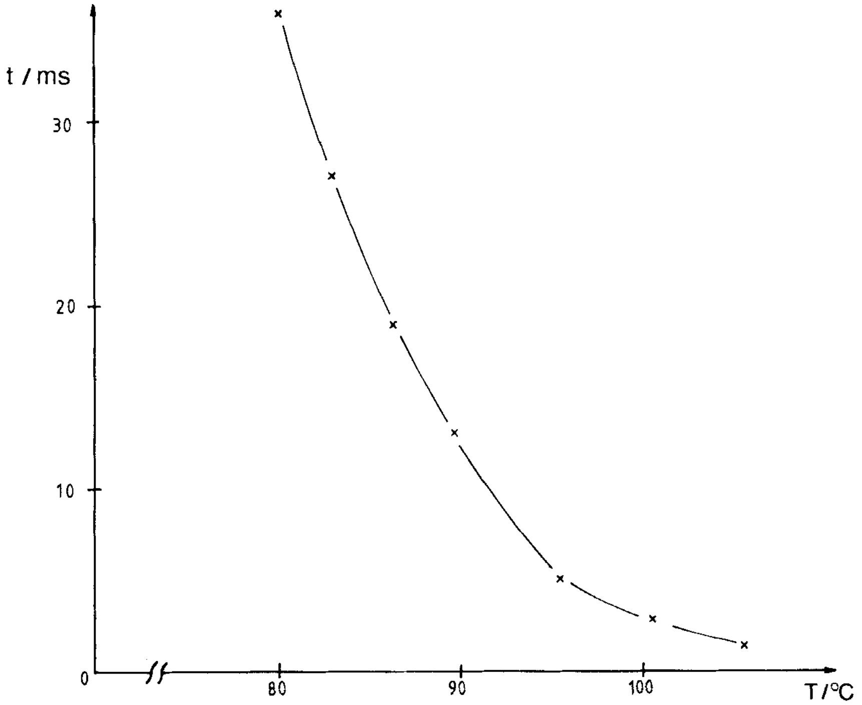


Figure 8. Temperature dependence of the response time of polymer **16** in a 2 μm cell at 25 V.

2.4. *Structural variations of polymer* **14**

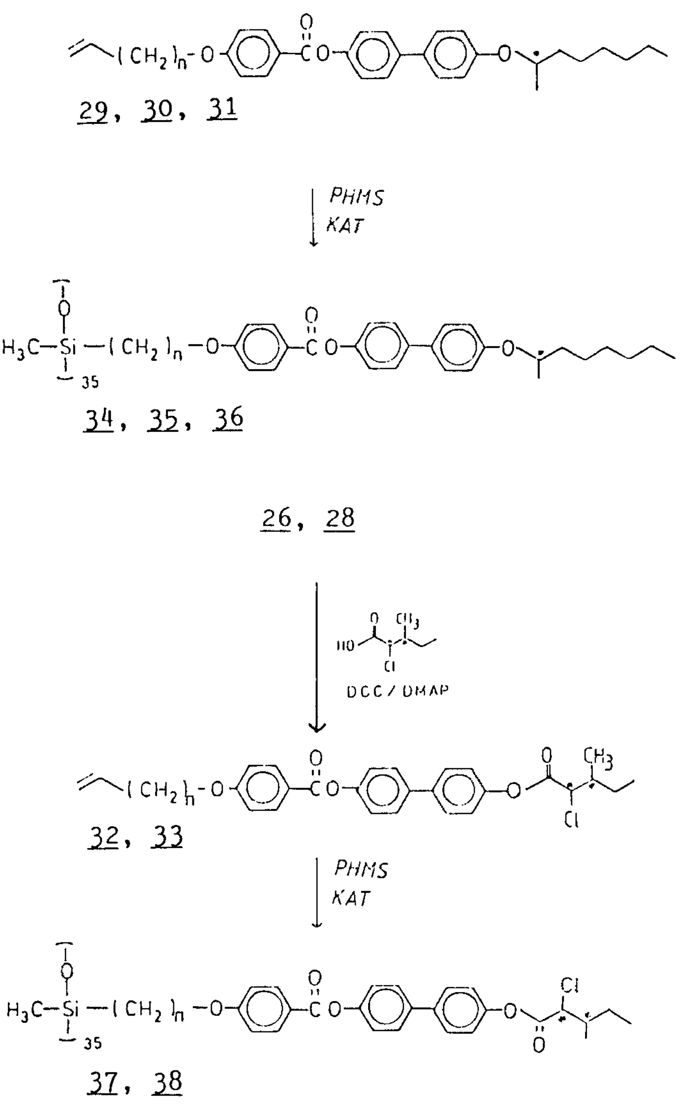
How does the length of the spacer between main chain and smectogenic unit influence the switching ability? To answer this question the spacer length in polymer **5** was reduced to eight methylene groups. Polymer **15** forms only two mesophases, which have not yet identified. **15** does not show any switching in D.C. fields.

However, another fast switchable polymer of type **14** was found by changing the chiral moiety to the chloro ester function, which is known to cause high spontaneous polarization in ferroelectric liquid crystals. Polymer **16** is switchable in the temperature range of 80–105°C; a plot of the switching times versus the temperature is shown in figure 8. The response time varies between 2 and 36 ms at a D.C. field of 25 V. In this case the two stable states show slight changes in the texture when the field is switched off.

2.5. *Switchable polysiloxane side chain polymers*

As far as we are aware there has been no report of switchable polysiloxane side chain polymers. Due to their low lying glass transition temperatures polysiloxane liquid-crystalline polymers are expected to be favourable candidates for fast switching ferroelectric polymers operating at about room temperature. The goal of this part of our work was to realize these compounds by using the same smectogenic side group, which proved to be advantageous to obtain switchable polymers such as **14** and **16**.

The mesogenic alkenes **29–31** differing only in the length of their flexible spacers were synthesized using the procedure for monomer **5** outlined in scheme 1. **32** and **33** were obtained as shown in scheme 3. Polymers **34–38** were obtained by platinum catalyzed polymer analogous reaction of poly(methylhydrogensiloxan) ($PHMS_{35}$) with the mesogenic alkenes **29–33**. **34–36** exhibit two mesophases, whereas **37** and **38** containing the chiral chloro ester unit do not show liquid-crystalline properties. In



Scheme 3.

table 3 the transition temperatures of the mesogenic alkenes and the derived polysiloxanes are compared.

Polysiloxanes **34–36** are swichtable by D.C. fields. Due to their viscosity they do not drawn in to thin cells (4 μm) by capillary attraction. In 25 μm cells after annealing for some time in electric fields domains develop, which can be switched between dark and bright states at D.C. fields of 30 V. The switching process in polymer **35** is observable between 80 and 150°C. The response time is ~200 ms at 130°C.

3. Experimental part

The complete experimental part including the synthetic procedure for compounds **1–38** and their characterization by ^{1}H N.M.R. (400 MHz) data and optical rotation has been deposited at the British Library, Document Supply Centre, Boston Spa,

Table 3. Transition temperatures (in °C) of mesogenic alkenes (**A**) and derived polysiloxanes (**P**).

No.									Switchable
A **29**	C 61·7	S_B 66·7		S_C^* 101·7	S_A 105·6	N* 114·6	BP_I 116·0	BP_{II} 116·1 I	+
P **34**		S_I 66	S_2 172 I						+
A **30**		S_X 53·8		S_C^* 75·6	S_A 79·1	N* 101·8	BP_I 104·5	BP_{II} 104·7 I	+
P **35**		S_I 72	S_2 155 I						+
A **31**	C 44·9			S_C^* 76·2		N* 104·9	BP_I 107·6 I		+
P **36**		S_I 111	S_2 170 I						+
A **32**	C 84·0			S_C^* 130·0	S_A 139·8	N* 153·9	BP_I 154·4	BP_{II} 154·7	+
P **37**	T_G 250 I								−
A **33**	C 64·3	S_X 92·1		S_C^* 112·8	S_A 116·1	N* 164·4	BP_I 165·0	BP_{II} 165·1 I	+
P **38**	T_G 248 I								−

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The liquid crystal transition temperatures of the compounds were determined by optical microscopy using an Olympus BH-2 in conjunction with a Linkam THN-60 heating stage and a TMS 90 control unit. The liquid crystal transition temperatures were also determined using a Mettler TA-2000. The purity of the compounds were determined by thin layer chromatography and G.P.C., Column chromatography was carried out using Merck silica-gel 60 (0·040–0·063). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Optical rotations were taken on a Perkin-Elmer 141 polarimeter. N.M.R. spectra were recorded at 400 MHz (Bruker WM 4000).

(1″R)-(+) 4′-(1-methyl-heptyloxy)-4-biphenylyl 4-(11-acryloyloxy-undecyloxy)-benzoate **7**. To a solution of **6** (3 g, 5 mmol) and triethylamine (1·4 ml, 10 mmol) in 50 ml dry THF, acryloylchloride (0·65 ml, 8 mmol) was added dropwise at 0°C. The mixture was stirred for 1 h at room temperature. The white precipitate was dissolved in water and the mixture was extracted with dichloromethane (3 × 30 ml). The combined organic layers were washed with a dilute solution of Na_2CO_3 (30 ml), water (10 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by F.C. on silica-gel using dichloromethane/petroleum ether as eluent. Yield: 2·7 g (84 per cent), $|\alpha|_{\mathrm{D}}^{25} = +3{\cdot}3$ ($c = 0{\cdot}40$, $CHCl_3$). For the transition temperatures see table 1.

^{1}H-N.M.R. (400 MHz, $CDCl_3$): $\delta = 0{\cdot}88$ (*t*, $J = 7$ Hz; 3 H), 1·20–1·54 (*m*; 22 H), 1·32 (d, $J = 6$ Hz; 3 H), 1·58 (m; 2 H), 1·67 (tt, $J = 7$ and 7 Hz; 2 H), 1·82 (tt, $J = 7$ and 7 Hz; 2 H), 4·05 (t, $J = 7$ Hz; 2 H), 4·16 (t, $J = 7$ Hz; 2 H), 4·40 (tq, $J = 6$ and 6 Hz; 1 H), 5·82 (dd, $J = 10$ and 1·5 Hz; 1 H), 6·12 (dd, $J = 17$ and 10 Hz; 1 H), 6·40 (dd, $J = 10$ and 1·5 Hz; 1 H), 6·95, 7·58 (AA′BB′, J(AB) = 8·5 Hz; 4 H), 6·98, 8·16 (AA′BB′, J(AB) = 8·5 Hz; 4 H), 7·24, 7·50 (AA′BB′, J(AB) = 8·5 Hz; 4 H).

(2S, 3S)-(+) 4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-acryloyloxy-decyloxy)-benzoate **13**. A solution of **10** (1·7 g, 3·3 mmol), (2*S*, 3*S*)-2-chloro-3-methylpentanoic acid [11] (555 mg, 3·7 mmol), DCC (762 mg, 3·7 mmol) and DMAP (50 mg) in 20 ml dry dichloromethane were stirred at room temperature for 24 h and then filtered to remove precipitated material. The filtrate was evaporated under reduced pressure and the solid residue purified using F.C. on silica-gel with dichloromethane/petroleum ether 1/1 as eluent. Yield: 1·16 g (54 per cent), $|\alpha|_{\mathrm{D}}^{25} = +4{\cdot}2°$ (c = 0·073, $CHCl_3$). For the transition temperatures see table 1.

^{1}H-N.M.R. (400 MHz, $CDCl_3$): $\delta = 1{\cdot}00$ (t, $J = 7$ Hz; 3 H), 1·16 (d, $J = 7$ Hz; 3 H), 1·29–1·52 (m; 12 H), 1,63–1·87 (m; 6 H), 2·24 (m; 1 H), 4·05 (t, $J = 7$ Hz; 2 H), 4·15 (t, $J = 7$ Hz; 2 H), 4·40 (d, $J = 7$ Hz; 1 H), 5·82 (dd, $J = 10$ and 1·5 Hz; 1 H), 6·12 (dd, $J = 17$ and 10 Hz; 1 H), 6·40 (dd, $J = 17$ and 1·5 Hz; 1 H), 6·98, 8·16 (AA′BB′, J(AB) = 8·5 Hz; 4 H), 7·20, 7·60 (AA′BB′, J(AB) = 8·5 Hz; 4 H), 7·28, 7·60 (AA′BB′, J(AB) = 8·5 Hz; 4 H).

Poly-(1‴R)-(+) 11-undecyl-[4″-(1-methyl-heptyloxy)-4′-biphenylyloxycarbonyl-4-phenoxy] acrylate in **14**. The monomer **7** was polymerized with AIBN (2·8 mg, $1{\cdot}7 \times 10^{-3}$ mmol) 9 ml dry THF solution and a N_2 atmosphere. The polymerization was carried out at 60°C for 24 h. The polymer was purified by reprecipitation from concentrated THF solution with methanol, at least three times. Yield: 538 mg (49 per cent), $|\alpha|_{\mathrm{D}}^{25} = +1{\cdot}8°$ (c = 0·19, $CHCl_3$).

Poly-(2S, 3S)-(+) 10-decyl-[4″-(2-chloro-3-methylpentanoyloxy)-4′-biphenylyloxy-carbonyl-4-] acrylate **16**. Yield: 412 mg (48 per cent), $|\alpha|_D^{25} = +2{\cdot}4°$ (c = 0·18, $CHCl_3$). The ^1H N.M.R. spectra of the polyacrylates show a characteristic line broadening.

Polymethyl-(1‴R)-(+)-10-[4″-(1-methyl-heptyloxy)-4′-biphenylyl-oxycarbonyl-4-phenoxy]-decylsiloxane **34**. To a mixture of polyhydrogen-methylsiloxane ($PHMS_{35}$) (68 mg, 1·07 mmol Si-H) and **29** (890 mg, 1·6 mmol) in 60 ml dry toluene, a solution of H_2PtCl_6 (0·1 ml, 2×10^{-4} mmol) in 2-propanol was added. The mixture was heated under reflux for 48 h. After cooling to room temperature, the polymer was isolated by precipitation with methanol, it was then redissolved in THF and five times further precipitated with methanol and dried *in vacuo*. Yield: 280 mg (43 per cent), $|\alpha|_D^{25} = 0{\cdot}7°$ (c = 0·10, $CHCl_3$).

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