Low transition temperature organosiloxane liquid crystals displaying a de Vries smectic A phase

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The synthesis, phase properties and electro-optic response of two new chiral low molar mass organosiloxane liquid crystalline materials are presented. The structure of the molecule contains a short (three silicon atoms) siloxy chain attached via a hydrocarbon chain to the non-chiral end of a chiral mesogenic moiety. The materials have low melting points ($< -20°C$) and broad smectic phase ranges ($\sim 80°C$ wide) extending to below room temperature. Both materials are electroclinic at room temperature. A $30°$ tilt of the optic axis can be achieved in fields of the order of 25 V μm^{-1}. The data presented indicate that in these materials the smectic phase is a de Vries-type smectic A phase. The electroclinic effect arises because the electric field produces a bias in the distribution of the direction of the tilt.

1. Introduction

A substantial research effort is currently invested in the development of liquid crystal materials exhibiting wide room-temperature chiral smectic C (SmC*) or chiral smectic A (SmA) phases. These ferroelectric (FLC) or electroclinic materials have great potential for applications in electro-optic devices ranging from large area flat-panel displays [1], ultra fast electro-optic modulators [2], and spatial light modulators [3–5].

Electroclinic materials are prime candidates for electro-optic applications where grey scale capability and fast dynamic response are required. The limiting features of electronic materials for use in applications thus far have been the low induced tilt angles that result in low contrast ratios and narrow temperature range of the SmA phase at temperatures around ambient.

In most electroclinic and ferroelectric materials the terminal tail groups of the molecules are hydrocarbon chains. However, recently there has been some effort to study the effect of replacing the alkyl chains partially with either fluorocarbons or siloxy units [6–8]. The partial substitution of alkyl chains by more flexible dimethyl-siloxane groups is expected to enhance the temperature

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range of the smectic phases and to lower the transition temperatures of the liquid crystal materials [7–9]. Dimethylsiloxane groups are bulky and exhibit more irregular conformations than their alkyl chain counterparts; one may therefore expect a reduced coupling between the mesogenic moieties within a layer or between the mesogenic moieties in adjacent layers. A reduced coupling of the mesogens favours the formation of a de Vries-type SmA phase [10]. However, the layered structure of the phase that is driven by the micro-separation of the siloxane moieties is stable over a broad temperature range. De Vries-type smectic A phases are ideal for electroclinic applications. In these materials, the molecules are tilted with respect to the layer normal but there is no long range correlation in the directions of tilt [10]. The average optic axis of the material is therefore normal to the layers. The application of an electric field produces a bias in the distribution of the directions of the molecular tilt with a concomitant tilt of the average optic axis. The tilt of the optic axis increases with field and saturates at a value equal to the molecular tilt [10, 11]. Throughout the remainder of this paper the term de Vries-type smectic A phase is used in a rather loose sense meaning that in the smectic phase there is no long range correlation between the directions of tilt of the mesogens. The experimental methods presented here are based on observations

of the orientation of the average optic axis and therefore do not permit us to infer whether the lack of correlation is within the layer or between layers.

Two new low molar mass organosiloxane materials TSiKN65F and TSi10PPBN4 are presented. These materials are homologous to the materials described in references [6, 10, 11]; they both exhibit a low melting point ($< -20°$C) and a wide temperature range of chiral smectic phase that includes room temperature; they display a de Vries-type smectic A phase at room temperature [12].

2. Experimental
2.1. *General*

All reactions were performed under a positive pressure of nitrogen using standard manifold techniques unless otherwise stated. Analytical thin layer chromatography was performed on glass silica plates (0.25 mm thick E. Merck silica gel 60-F254), using the solvent mixtures indicated. Preparative chromatographic purifications were performed by employing flash chromatography on E. Merck 40–63 μm normal phase silica gel.

Dry THF, dichloromethane and toluene were used as received from Fluka, as were diethyl azodicarboxylate, triphenylphosphine, and bromohexene. Heptamethyl-trisiloxane was obtained from Gelest.

300 MHz ^{1}H NMR spectra were recorded on a Bruker MSL300 spectrometer in CDCl$_3$ or DMSO solutions. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY).

2.2. *Material synthesis*

The synthesis steps for the preparation of the chiral liquid crystalline compounds with the siloxy end tail group are illustrated in schemes 1 and 2.

The fluorobenzoic acid derivative **3** was prepared by reacting 3-fluoro-4-hydroxybenzoic acid with bromo-hexene in the presence of potassium hydroxide and ethanol. The vinylic derivative **5** was obtained by reaction of the acid chlorides of **3** and **4** in the presence of NaH. The corresponding siloxy liquid crystalline materials were obtained through the classical hydrosilylation reaction [13] between the vinyl mesogenic groups **5** or **9** and heptamethyltrisiloxane in the presence of a Pt-catalyst.

2.2.1. *3-Fluoro-4-(5-hexenyloxy)benzoic acid (3)*

Compound **1** (5 g, 32.05 mmol) was added to a solution of KOH (4.48 g, 80.01 mmol) in 100 ml of 90% ethanol. Potassium iodide (0.1 g) was added and the solution was heated to 85°C for 1 h. Bromohexene (7.33 g, 45 mmol) was slowly added and the solution heated under reflux overnight. The solution was cooled and acidified with 6N HCl solution. The crude product was obtained by

filtration and recrystallized from acetic acid/water; Yield 5 g (65%). ^{1}H NMR (DMSO, TMS) δ (ppm): 1.30–1.98 (m, 6H, (CH$_2$)), 3.94 (t, 2H, CH$_2$O), 5.01 (m, 2H, CH=CH$_2$), 5.71 (m, 1H, CH=CH$_2$), 6.96 (d, 1H, ArH), 7.73 (s, 1H, ArH), 7.79 (d, 1H, ArH), 11.0 (s, 1H, COOH). Anal: calcd for C$_{13}$H$_{15}$FO$_3$ C 65.53, H 6.35; found C 65.40, H 6.17%.

2.2.2. *4'-{[(1R)-1-Methylhexyl]oxy}-3'-nitro-[1,1'-biphenyl]-4-yl 3-fluoro-4-(5-hexenyloxy)-benzoate (5)*

A mixture of **3** (200 mg, 0.92 mmol) and excess of oxalyl chloride in benzene was stirred for 4 h at room temperature. The solvent was evaporated and the crude acid chloride used directly in the coupling reaction without further purification. A suspension of NaH (23 mg, 0.94 mmol) in 6 ml of dry THF was added to a solution of **4** (305 mg, 0.93 mg) in 10 ml of THF under nitrogen. A solution of the acid chloride in THF prepared above was added dropwise to the reaction mixture which was stirred for 24 h at room temperature. The reaction was quenched by addition of water, and the resulting aqueous phase extracted with ether (3 times). The combined organic phases were washed with 10%HCl, 5%NaOH and brine, and dried over sodium sulfate. The solvent was evaporated and the crude product purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 85/15) to give **5** in 80% yield. ^{1}H NMR (CDCl$_3$, TMS) δ (ppm): 0.91 (t, 3H, $^-$CH$_2$CH$_3$); 1.3–1.98 (m, 14H); 1.31 (d, 3H, $^-$CHCH$_3$); 3.94 (t, 2H, CH$_2$O); 4.48 (m, 1H, CHCH$_3$); 5.01 (m, 2H, CH=CH$_2$); 5.71 (m, 1H, CH=CH$_2$); 6.96 (d, 1H, ArH); 7.73 (s, 1H, ArH); 7.79 (d, 1H, ArH); 7.76 (dd, 1H, ArH); 7.1 (d, 1H, ArH); 7.25 (d, 2H, ArH); 7.56 (d, 2H, ArH); 8.1 (1H, d, ArH). Anal: calcd for C$_{32}$H$_{36}$FNO$_6$ C 69.93, H 6.60, N 2.55; found C 69.80, H 6.50, N 2.32%.

2.2.3. *4'-{[(1R)-1-Methylhexyl]oxy}-3'-nitro-[1,1'-biphenyl]-4-yl 3-fluoro-4-(6-heptylmethyl-trisiloxyhexyloxy)benzoate (6)*

To a solution of heptamethyltrisiloxane (218 mg, 0.98 mmol) and (500 mg, 0.91 mmol) of **5**, dissolved in 20 ml of dry THF, were added 5 mg of dicyclopentadienyl-plantinium(II) chloride catalyst. The reaction mixture was stirred at 60°C under nitrogen for 24 h. The solvent was removed and the crude product purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 90/10) to give **6** in 70% yield. ^{1}H NMR (CDCl$_3$, TMS) δ (ppm): 0.02 (s, 6H, CH$_2$$^-$Si(CH$_3$)$_2$); 0.1 (s, 9H, Si(CH$_3$)$_3$); 0.15 (s, 6H, O$^-$Si(CH$_3$)$_2$$^-$O); 0.5 (m, 2H, CH$_2$$^-$Si); 0.91 (t, 3H, $^-$CH$_2$CH$_3$); 6.96 (d, 1H, ArH); 7.73 (s, 1H, ArH); 7.79 (d, 1H, ArH); 7.76 (dd, 1H,

Scheme 1.
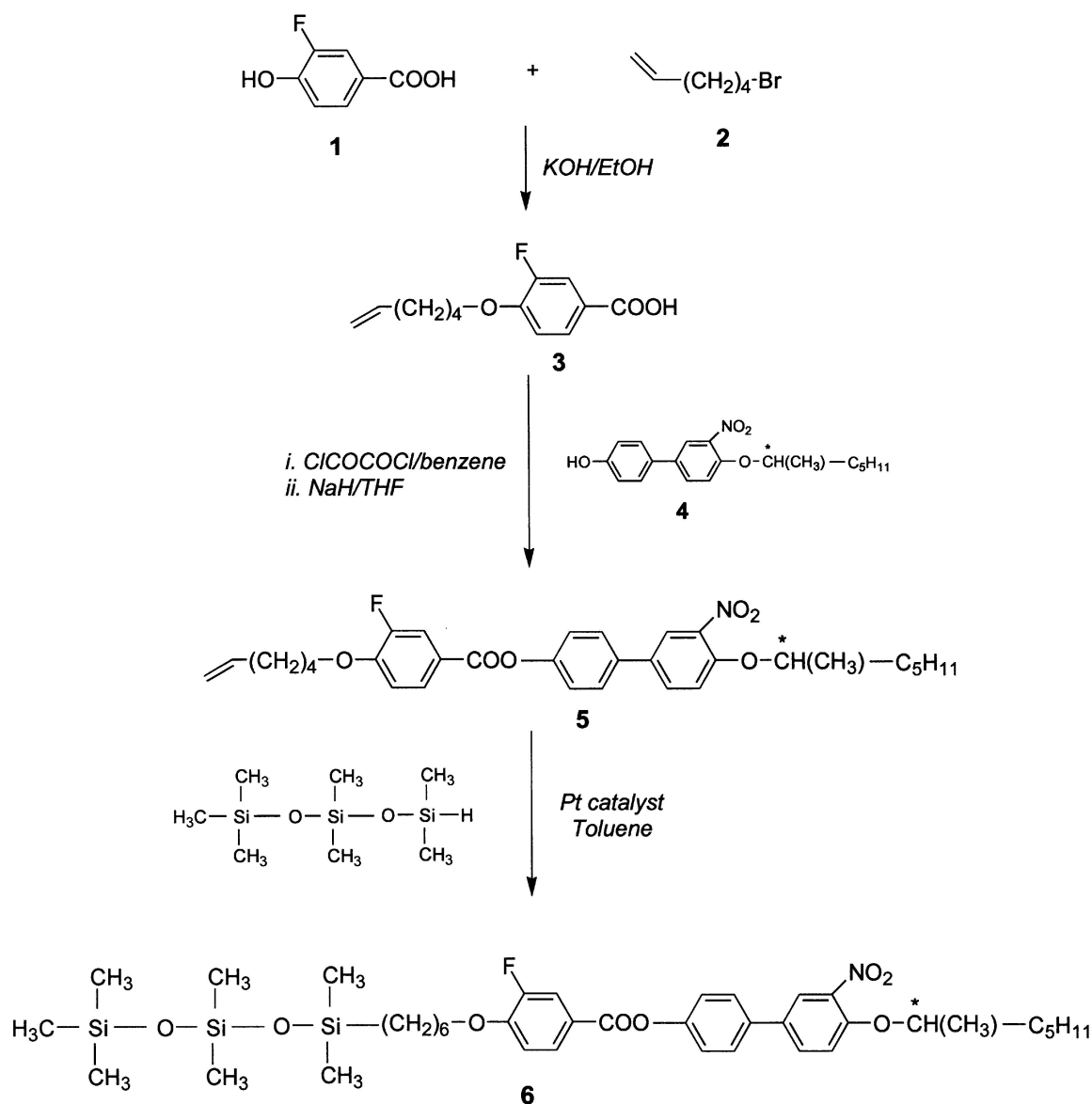
ArH); 7.1 (d, 1H, ArH); 7.25 (d, 2H, ArH); 7.56 (d, 2H, ArH); 8.1 (1H, d, ArH). Anal: calcd for $C_{39}H_{58}FNO_8Si_3$ C 60.67, H 7.57, N 1.81; found C 60.50, H 7.48, N 1.90%.

2.2.4. 4-[(R)-1-(Butoxycarbonyl)ethoxy]-3-nitrophenyl 4-[4-(5-hexynyloxy)phenyl]benzoate (9)

The synthesis of compounds **7** and **8** has been described elsewhere [14]. Compound **9** was prepared following the same procedure as for **5**. ^{1}H NMR (CDCl$_3$, TMS) δ (ppm): 1.2 (t, 3H, $-CH_2-CH_3$); 1.27 (m, 2H, $-CH_2-CH_3$); 1.5 (m, 9H); 2.1 (m, 2H, $CH_2-CH=C$); 4.0 (t, 2H, $-CH_2-OAr$); 4.25 (m, 2H, $-O-CH_2-CH_2$); 4.85 (q, 1H, $-CH-CH_3$); 4.98 (m, 2H, $CH_2=CH-$); 5.9 (m, 1H,

$CH_2=CH-$); 6.98 (dd, 2H, ArH); 7.48 to 7.90 (m, 8H, ArH); 8.14 (dd, 1H, ArH). Anal: calcd for $C_{32}H_{35}NO_8$ C 68.43, H 6.28; N 2.49; found C 68.55, H 6.14, N 2.38%.

2.2.5. 4-(2-Butoxy-1-methyl-2-oxoethoxy)-3-nitrophenyl 4'-(6-heptylmethyltrisiloxyhexxyloxy) 1,1'-biphenylcarboxylate (10)

Compound **10** was prepared following the same procedure as for **6**. Anal: calcd for $C_{39}H_{57}NO_{10}Si_3$ C 59.74; H 7.33, N 1.79; found C 59.84, H 7.20, N 1.85%. ^{1}H NMR (CDCl$_3$, TMS) δ (ppm): 0.02 (s, 6H, $-Si(CH_3)_2$; 0.1 (s, 9H, Si(CH$_3$)$_3$); 0.15 (s, 6H, O$-$Si(CH$_3$)$_2-$O); 0.5 (m, 2H, CH$_2-$Si); 1.2 (t, 3H, $-CH_2-CH_3$); 1.27 (m, 2H,

Scheme 2.
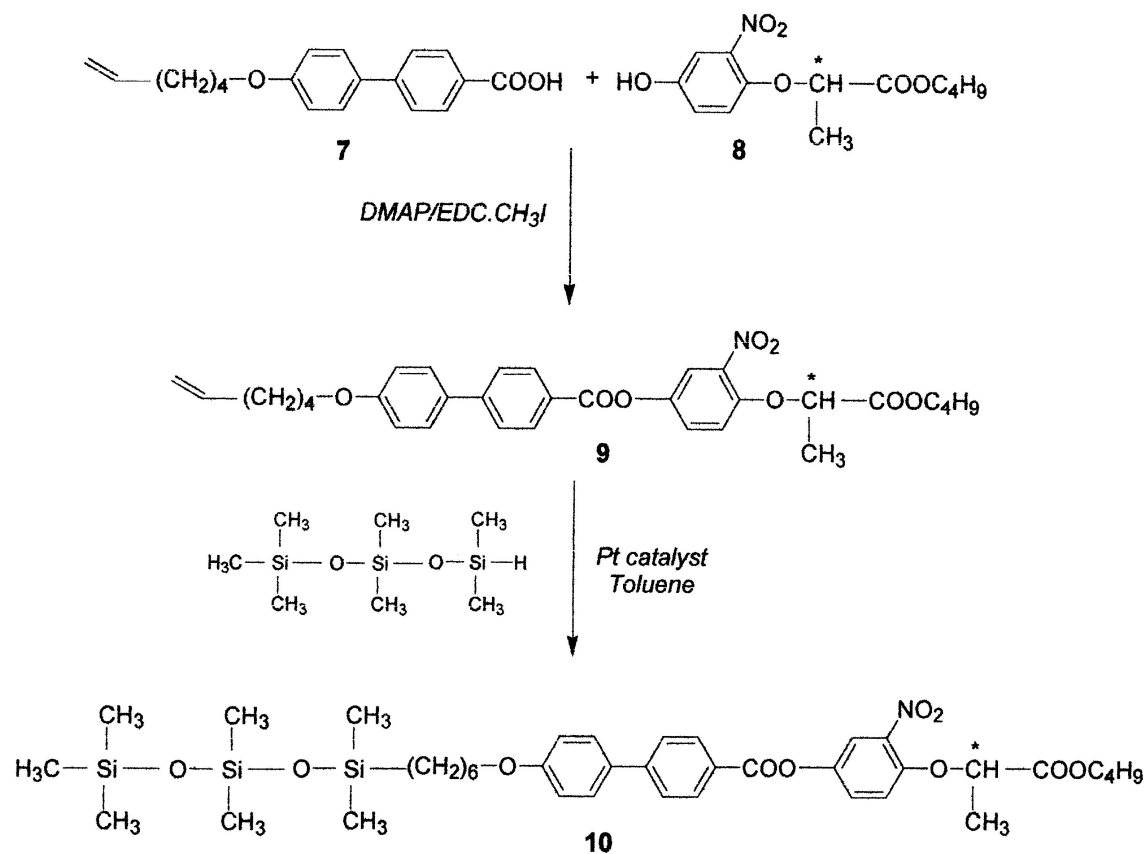
−CH$_2$−CH$_3$); 1.5 (m, 13H); 4.0 (t, 2H, −CH$_2$−OAr); 4.25 (m, 2H, −O−CH$_2$−CH$_2$); 4.85 (q, 1H, −CH−CH$_3$); 6.98 (dd, 2H, ArH); 7.48 to 7.90 (m, 8H, ArH); 8.14 (dd, 1H, ArH).

3.   Characterization of the materials and discussion

The phase sequences and transition temperatures were determined by polarizing optical microscopy (POM) and by observing the electro-optic response of the materials. The measurements of the electric field-induced tilt angle and of the response time were made on 5 μm thick uniformly aligned specimens contained in glass cells equipped with transparent ITO electrodes. The inner face of the cell was treated with rubbed polyimide to foster planar alignment of the material. A uniform alignment was obtained by slowly cooling (2°C min^{-1}) the specimen in the presence of a bi-polar triangular wave (30 Hz and 80 V$_{pp}$). The tilt of the optic axis was determined as half the angle between two positions of optical extinction when the sample is switched between crossed polarizers. The two positions of optical extinction were observed by eye using POM with a rotation stage. A low frequency (50–100 mHz) bipolar square wave was applied to the specimen to switch the material between the two positions. The response times quoted in this

paper are the optical response times; they are the time required for the intensity of the transmitted light to change from 10% to 90% when the specimen is switched between crossed polarizers. The temperature dependence of the physical properties was measured with an accuracy of 0.2°C using a heating–freezing stage and a temperature controller from Linkam Ltd (UK).

3.1. *Mesophase behaviour*

The phase transition temperatures of the materials are shown in the table. On cooling, both materials TSiKN65F and TSi10PPBN4 show a transition from the isotropic phase directly into a smectic phase. This is usually the case with low molar mass organosiloxane materials [7, 8]. The materials remain smectic until temperatures as low as −30°C. At low temperatures a

Table 1.   Phase sequences of the materials as observed by optical microscopy.

Specimen	Phase sequence
TSiKN65F	Cr $\xleftrightarrow{\approx-35°C}$ SmA$_{deVries}$ $\xleftrightarrow{68°C}$
TSi10PPBN4	Cr $\xleftrightarrow{\approx-34°C}$ S$_C^*$ $\xleftrightarrow{23°C}$ SmA$_{deVries}$ $\xleftrightarrow{100°C}$

sharp increase in the response time of the material to an electric field is observed. This behaviour is likely to be due to an increase in the viscosity of the material before a transition to a glassy phase.

It appears from the electro-optic response described in the next section that the smectic phase is a de Vries-type smectic A phase, which has been observed [10, 15] in the homologous material TSiKN65. At lower temperatures the specimen TSi10PPBN4 display a transition to a SmC* phase whereas TSiKN65 remains in a de Vries-type smectic A phase.

3.2. *The electric field-induced tilt of the optic axis*

A strong electroclinic effect is observed in both materials. It is emphasized that in a de Vries-type smectic A phase the observed electric field-induced tilt of the optic axis is not due to a change in the tilt of the molecules but to a bias of the random distribution of the directions of tilt towards the orientation favored by the electric field [10, 12, 15]. The variation of the field-induced tilt of the optic axis as a function of the applied field at different temperatures for TSiKN65F and TSi10PPBN4 is shown in figures 1 and 2 respectively. The large initial value of the electroclinic effect and then a saturation at high fields are expected from a de Vries-type smectic A phase [10, 12, 15].

In both materials, we observe a threshold field below which the electroclinic effect is negligible. The threshold field is defined as shown in figure 3 as the intersection of the linear portion of the graph with the field axis. The value of the threshold field increases with increasing temperature. The origin of this threshold is still under investigation and will be reported separately [16]. The material TSiKN65F displays an electroclinic behaviour
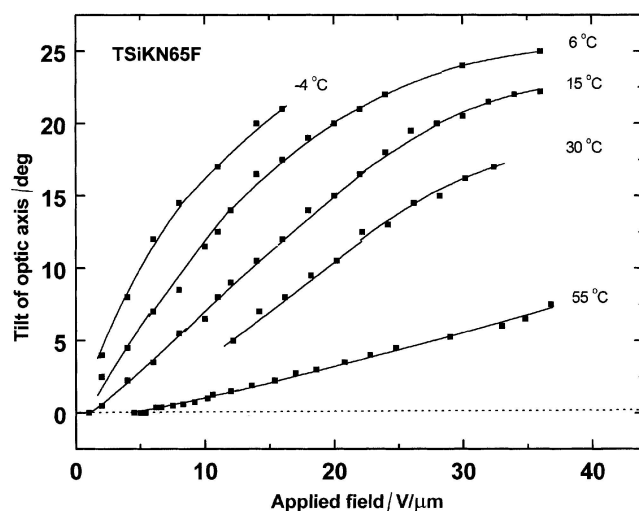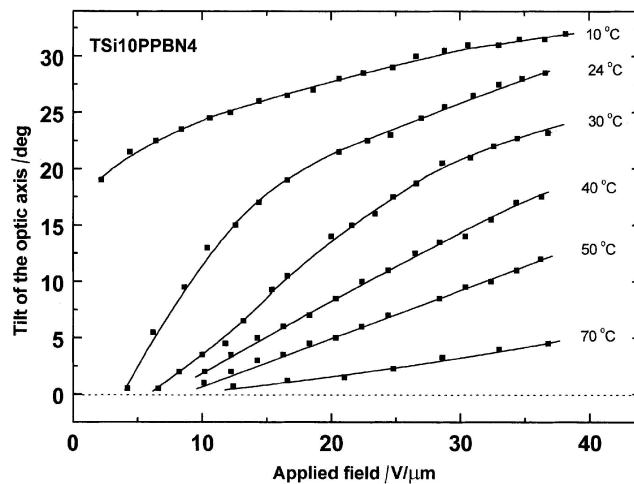

Figure 2. The induced tilt of the optic axis as a function of the applied field in TSi10PPBN4 at selected temperatures. The solid lines are a guide to the eye. At 10°C there is a spontaneous tilt of the optic axis in zero field.
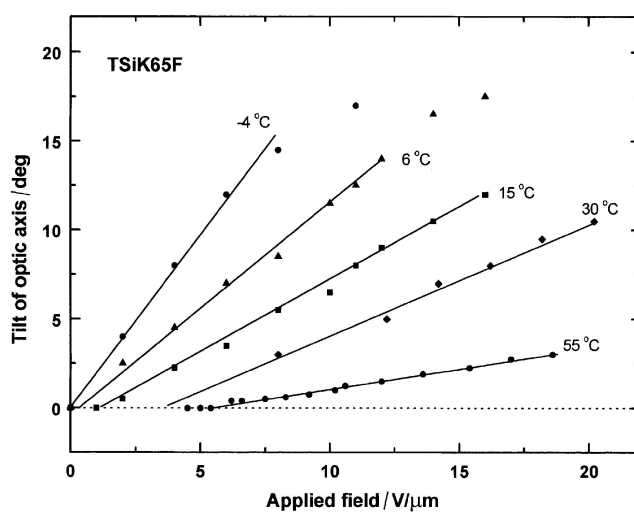

Figure 3. The induced tilt of the optic axis at low fields in TSi10PPBN4. The threshold field is defined as the intersection of the linear portion of the graph with the field axis. The electroclinic coefficient is taken as the slope of the linear portion of the graph.

down to the lowest temperatures (−30°C) investigated. For the material TSi10PPBN4 at 10°C, the extrapolation of the curve to zero field gives a tilt angle of about 17°. This is much smaller than the saturation angle (>30°) at high fields. These observations could be interpreted by saying that at this temperature there is a spontaneous bias of the distribution of the directions of tilt towards a preferred direction; the distribution becoming more peaked as the temperature is reduced. However, we have not observed any significant tilt of the optic axis when the specimen is cooled in the absence of any electric field. This would suggest that the behaviour of this
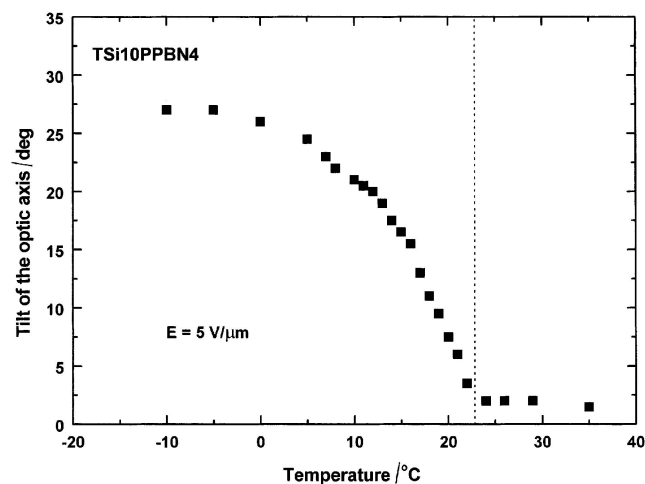

Figure 1. The induced tilt of the optic axis as a function of the applied field in TSiK65F at selected temperatures. The solid lines are a guide to the eye.

Figure 4. The variation of the tilt of the optic axis as a function of temperature, the measuring field is a 5 V μm^{-1} d.c. field.
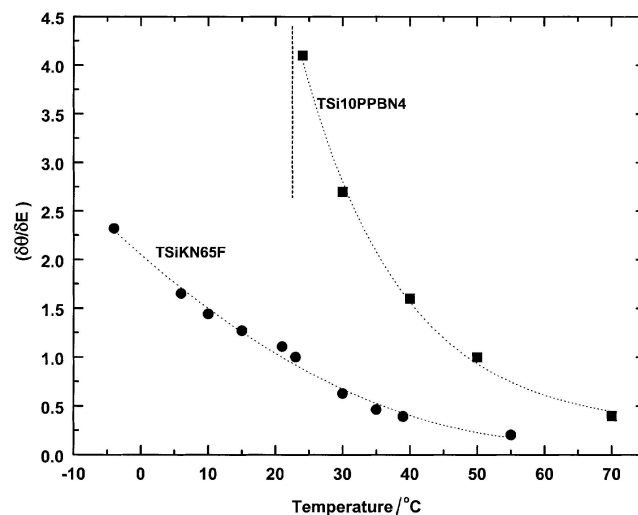

Figure 5. The variation of the electroclinic coefficient as a function of temperature. The dashed line indicates the temperature of the onset of the spontaneous tilt of the optic axis in TSi10PPBN4.

material could be that of a highly sensitive 'V-shaped' response as proposed by the Boulder Group.† A detailed study of the physical properties of TSi10PPBN4 is under way and will be reported in [16].

The temperature dependence of the tilt of the optic axis measured with a field of 5 V μm is given in figure 4. The transition temperature quoted in the table corresponds to the onset of the electro-optic response.

An electroclinic coefficient can be defined here as the slope of the linear portion of the graph of induced tilt versus field. The behaviour of the electroclinic coefficient as a function of temperature for TSiKN65F and for TSi10PPBN4 is shown in figure 5. In both materials the electroclinic coefficient increases as the temperature is lowered. In TSi10PPBN4 the electroclinic coefficient appears to diverge at the temperature where the spontaneous bias in the distribution of the directions of tilt is observed. Such behaviour is expected since at lower temperatures there is a larger correlation between the directions of tilt of molecules.

3.3. *Response time*

The behaviour of the optical response time is very much the same in both materials. At room temperature and above, the response time is of the order of 500 μs at high fields and increases sharply for fields less than 10 V μm^{-1}. The temperature dependence of the

† During the refereeing process, the Boulder Group has published a paper (*Appl. Phys. Lett.*, 2002, **80**, 4097) presenting a material displaying a similar behaviour. These authors obtain a satisfactory description of the behaviour using the BHL model. We are grateful to the referee for bringing to our attention the work of the Boulder Group.

response time at the fixed field of 33 V μm^{-1} is shown in figure 6. Although both materials have approximately the same crystallization temperature, the response time in TSiKN65F diverges at a higher temperature (by 10°) than in TSi10PPBN4. At temperatures below −20°C the response time is of the order of minutes. Note that TSi10PPBN4 displays no observable anomalies in the response time at the onset of the spontaneous tilt of the optic axis. The crystallization temperatures quoted in the table correspond to the temperatures when no response could be observed at the highest field (33 V μm^{-1}) available.
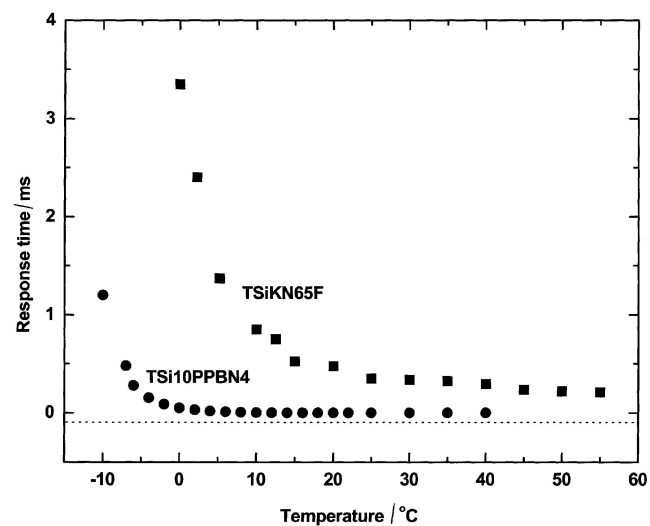

Figure 6. The optical response time as a function of temperature.

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