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## Liquid Crystals

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# Synthesis and characterization of novel ferroelectric liquid crystals and copolymers containing biphenyl azobenzene and/ or phenyl biphenyl carboxylate mesogenic groups

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Two new ferroelectric liquid crystals, 4-[(*S*)-1-(ethoxycarbonyl)]ethyl 4-[4'-(9-decenyloxy)-biphenyl]azobenzoate (**10**) and its ester analogue 4-[(*S*)-1-(ethoxycarbonyl)]ethyl {[4-(9-decenyloxy)]biphenyl-4'-yl}carbonyloxybenzoate (**17**), and side chain polysiloxane copolymers and terpolymers containing various amounts of **10** and **17** as mesogenic side groups have been synthesized. Their mesomorphic and physical properties have been characterized. Both **10** and **17** exhibit isotropic, SmA\*, SmC\*, and Sm(I or F)\* phases. The copolymer with **17** as the mesogenic group and terpolymers having low content of the azo compound **10** show a SmC\* phase over a large temperature range down to room temperature. The copolymer with the azo compound **10** as the mesogenic group is amorphous.

## 1. Introduction

Ferroelectric liquid crystals and ferroelectric liquid crystalline side chain polymers are the subject of intense investigation, due to the possibility of their use in displays and optoelectronic devices [1]. Fast switching between two stable orientations in the SmC\* phase is the key for the interest in this subject. In a significant paper, Ikeda *et al.* [2] showed that ferroelectric switching can be photochemically induced using a photo-isomerizable compound based on azobenzene. Taking advantage of the differences in the hysteresis curves (polarization as a function of electric field) of the *trans* and *cis* isomers of the azobenzene compound, the authors demonstrated that fast switching could be restricted to the parts of the cell which were illuminated (higher *cis* content), while the other parts were below the electric field threshold required for switching (*trans* isomers) and were left unchanged. This effect was achieved using the chiral azobenzene compound as a dopant in a

chiral SmC ester (3 mol%). The photo-induced shift in hysteresis curves indicates that a modulation of the spontaneous polarization ( $P_s$ ) is achieved by *trans-cis* photo-isomerization of the azobenzene component. This  $P_s$  photo-modulation effect has been observed in polymeric ferroelectric liquid crystals by Zentel *et al.* [3, 4] who demonstrated that *trans-cis* isomerization of an azobenzene side chain shifts the  $P_s$  vs. temperature curve towards lower temperatures, which can induce an order-disorder transition in a certain temperature range that is equivalent to an on-off switch.

A different approach to photo-modulation of  $P_s$  uses chiral photochromic dopants which maintain their rod-like shape in both *trans* and *cis* configurations. In this case,  $P_s$  photo-modulation is not accompanied by a destabilization of the ferroelectric liquid crystal phase [5, 6].

A phenomenon which makes use of the azobenzene *trans-cis* isomerization, but is fundamentally different, is the photo-induced orientation of azobenzene groups bound or doped into polymer matrices, under illumination with polarized light. The orientational direction is

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perpendicular to the light polarization and is produced by an isomerization and photo-selection process. For amorphous polymer systems, this is a disorder–order transition induced by light and has been proposed as a possible optical storage mechanism [7]. For liquid crystal polymers (smectic or nematic), in a previously oriented sample, the azobenzene orientation can be changed with polarized light (reorientation) [8]. Our research group is involved in the study of such orientation phenomena, and has started to investigate a possible combination of these two different phenomena: photo-modulation of  $P_s$  in azobenzene-containing ferroelectric liquid crystalline polymers, and photo-induced preferential orientation (possibly switching) produced by the existence of a preferred director (perpendicular to the light polarization). The ‘design’ of a suitable system involves the use of a typical ferroelectric liquid crystal, an azobenzene-based ferroelectric liquid crystal of a similar chemical structure, a polymer backbone of low glass transition temperature ( $T_g$ ) (to facilitate access to the chiral SmC phase around room temperature), and an appropriate polarity of the azobenzene group. The polarity is important because the azobenzene has to be part of a common liquid crystal phase with the other compound, thus the typical donor–acceptor substituted azobenzenes used in the orientation process are not of use here [9]. On the other hand, polarity is the dominant factor in the cooperative motion of groups which are inert to light but are moved in concert with the azobenzene groups, at least in amorphous systems [10].

In this paper, the synthesis and phase characterization of two new ferroelectric liquid crystals are presented: one is 4-[(*S*)-1-(ethoxycarbonyl)]ethyl 4-[4'-(9-decenyloxy)-biphenyl]azobenzoate, compound **10**, containing a transverse weakly donor–acceptor substituted biphenyl azobenzene chromophore which is expected to be photosensitive to visible laser light; the other is 4-[(*S*)-1-(ethoxycarbonyl)]ethyl {[4'-(9-decenyloxy)-biphenyl-4-yl]carbonyloxybenzoate, compound **17**, which is an ester analogue of **10**. The polysiloxane copolymers and terpolymers with various compositions of **10** and **17** are also described. We chose polysiloxane as the polymer backbone, because side chain ferroelectric liquid crystal polymers with this kind of backbone have been shown to exhibit chiral smectic C phases [11–13] even at room temperature.

## 2. Experimental

Melting points were determined on a Mel-tep II apparatus and are uncorrected. Absorption spectra were recorded on a Shimadzu UV160U UV-visible spectrophotometer. Proton NMR spectra were recorded on a Bruker AC-F 200 NMR spectrometer. Phase transition temperatures were measured by differential scanning

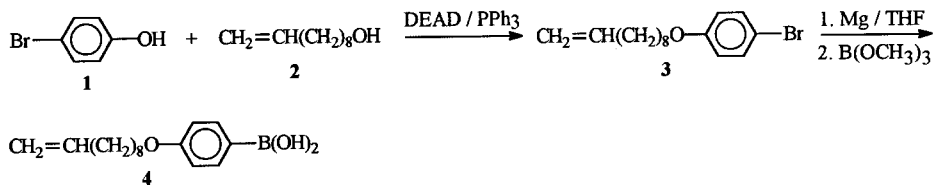
calorimetry (DSC) with a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head. The molecular weights (relative to polystyrene) of the resulting polymers were obtained by gel permeation chromatography (GPC) from a Water Associates liquid chromatography system equipped with a Model 440 absorbance detector and a Model R401 differential refractometer. Optical observations were made on a Nikon Labophot-2 polarizing microscope (magnification 200 $\times$ ) fitted with a RTC-1 temperature controller (Instec Inc., Broomfield, CO).  $P_s$  was measured by the triangular wave method [14] using a Displaytech Automated Polarization Testbed III (6 V  $\mu\text{m}^{-1}$ , 100 Hz) in conjunction with a RTC-1 temperature controller. Tilt angles ( $\theta_i$ ) were measured between crossed polarizers using a red cutoff filter ( $\lambda > 650$  nm) as half the rotation between two extinction positions corresponding to opposite polarization orientations. Polyimide-coated ITO glass cells (4  $\mu\text{m} \times 0.25$  cm<sup>2</sup>, both surfaces rubbed in a parallel direction) supplied by Displaytech Inc. (Longmont, CO) were used for all measurements. Elemental analyses were performed by Guelph Chemical Laboratories Ltd (Guelph, Ontario).

All reagents were obtained from commercial sources and used without purification unless otherwise noted. Dry dichloromethane and pyridine were obtained by distillation from CaH<sub>2</sub> prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under N<sub>2</sub>. 4-Bromophenol, 9-decen-1-ol, diethylazodicarboxylate (DEAD), trimethylborate, ethyl (*S*)-(-)-lactate, 4-nitrobenzoyl chloride, and 4-hydroxybenzoic acid were used as purchased from Aldrich. Poly[(30–35 mol %)-methylhydrosiloxane-co-(65–70 mol %)-dimethylsiloxane] ( $M_n = 2000$ –2100) was purchased from United Chemical Technologies Inc (Bristol, PA), and used as received. The average number molecular weight was determined by GPC and the value obtained was in agreement with the value given by the commercial source. The Pt-catalyst was synthesized following a reported procedure [15].

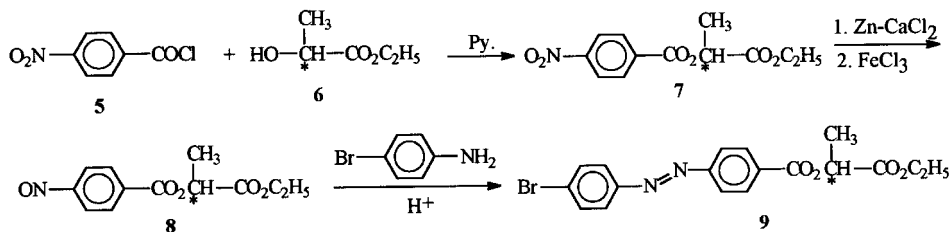
The following syntheses are illustrated in schemes 1–6.

### 2.1. 1-Bromo-4-(9-decenyloxy)-benzene (**3**)

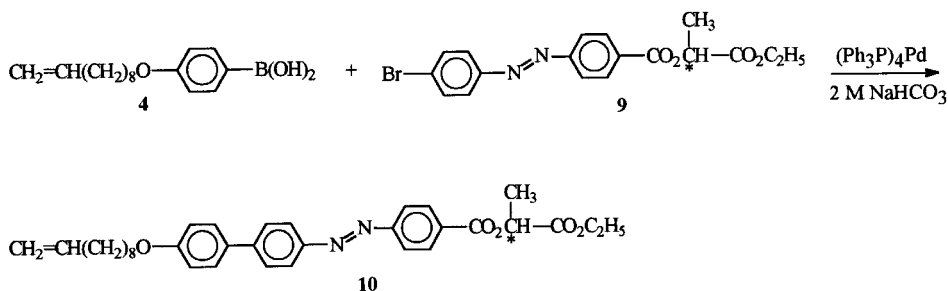
4-Bromophenol (5.19 g, 30 mmol), 9-decen-1-ol (5.53 ml, 31 mmol), and DEAD (4.87 ml, 31 mmol) were dissolved in dry THF (50 ml) under nitrogen and the resulting solution cooled to 0°C while stirring. A solution of triphenylphosphine (30 mmol) in dry THF (25 ml) was added dropwise to the cooled solution over approximately 20 min and the resulting mixture allowed to warm to room temperature. Stirring was continued for a further 48 h. The solution was evaporated to dryness, and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (200 ml); this solution was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to dryness. The residue was purified by silica



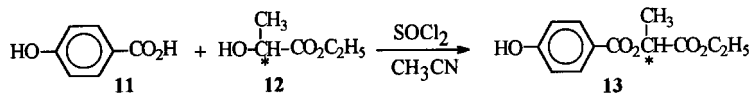
Scheme 1.



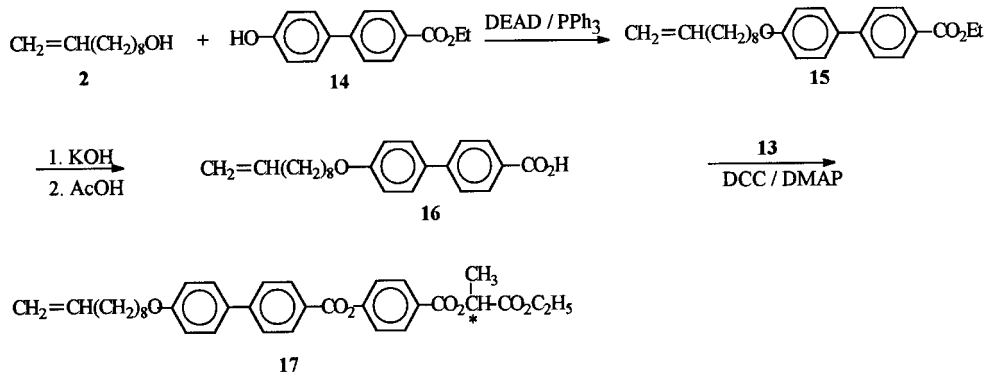
Scheme 2.



Scheme 3.



Scheme 4.

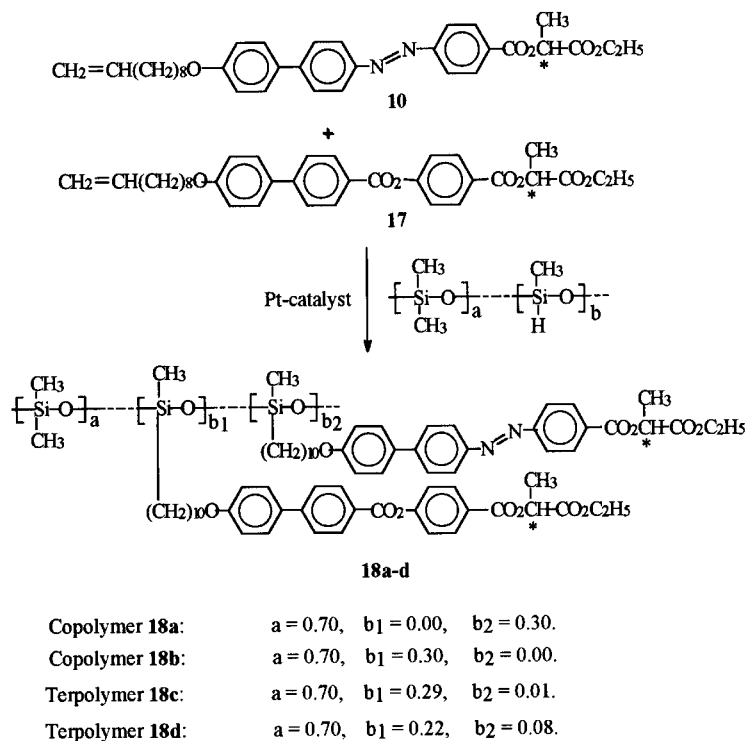


Scheme 5.

gel chromatography using 0–1% EtOAc in hexane as eluant to afford pure **3** (8.02 g, 86% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 1.15–2.12 (m, 14H, (CH<sub>2</sub>)), 3.85 (t, 2H, CH<sub>2</sub>O), 4.9 (m, 2H, CH=CH<sub>2</sub>), 5.32 (m, 1H, CH=CH<sub>2</sub>), 6.62 (dd, 2H, ArH), 7.30 (dd, 2H, ArH).

## 2.2. 4-(9-Decenyloxy)phenyl boronic acid (**4**)

Magnesium (0.384 g, 16 mmol) in dry THF (10 ml) was stirred under dry nitrogen at room temperature. Compound **3** (3.73 g, 12 mmol) was dissolved in dry THF (10 ml) and a few drops of this solution added to



Scheme 6.

the Mg/THF mixture. A small amount of iodine was added and the mixture warmed to reflux. Once the iodine colour had disappeared, the heat was removed and the remaining **3** in THF was added dropwise to achieve a continuous self-sustaining reflux of the reaction mixture. When addition was complete, heating under reflux was continued for a further 1.5 h. The reaction mixture was cooled on an ice-bath and trimethylborate (1.82 ml, 16 mmol) in dry THF (5 ml) was added slowly with stirring. The mixture was stirred for a further 30 min at 0–5°C. Dilute hydrochloric acid (10 ml, 20% v/v) was added carefully and the mixture stirred for 15 min at room temperature. The product was extracted into diethyl ether (60 ml) and the solution washed with water (2 × 40 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to dryness. Compound **4** was obtained as a white solid (3.04 g, 92% yield) which was used without further purification for the next step of the synthesis.

### 2.3. [(*S*)-1-(Ethoxycarbonyl)jethyl 4-nitrobenzoate (**7**)

A solution of 4-nitrobenzoyl chloride, **5** (8.35 g, 45 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added to a mixture of (*S*)-ethyl-lactate, **6** (5.67 ml, 50 mmol), 20 ml dry pyridine and 80 ml CH<sub>2</sub>Cl<sub>2</sub>. The resulting mixture was stirred at room temperature for 1 h. Then, 200 ml water and 100 ml CH<sub>2</sub>Cl<sub>2</sub> were added and the organic layer was washed with saturated aqueous NaHCO<sub>3</sub> (2 × 150 ml); it was then dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to dryness.

The residue was purified by silica gel chromatography using 8% EtOAc in hexane as eluant to afford pure compound **7** (11.29 g, 94% yield), m.p. 30–31°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 1.2 (t, 3H, CH<sub>2</sub>–CH<sub>3</sub>), 1.58 (d, 3H, CH–CH<sub>3</sub>), 4.18 (q, 2H, CH<sub>2</sub>–CH<sub>3</sub>), 5.26 (q, 1H, CH–CH<sub>3</sub>), 8.21 (s, 4 aromatic H).

### 2.4. 4-[(*S*)-1-(Ethoxycarbonyl)jethyl 4-(4-bromophenyl)azobenzoate (**9**)

A mixture of **7** (8.01 g, 30 mmol), 10 ml water, 60 ml ethanol and 0.3 g of CaCl<sub>2</sub> was heated to boiling with stirring, and then treated with 7.0 g of zinc dust (added slowly). After 15 min, the residue was filtered off and the solution poured into 320 ml water containing 9.8 g of ferric chloride cooled on an ice-bath. After stirring for 30 min, the product was extracted with diethyl ether, and the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to dryness to give the crude nitroso compound **8** (6.33 g, 87% yield) which was used for the next reaction without further purification.

A solution of **8** (5.5 g, 22 mmol), *p*-bromoaniline (4.162 g, 24.2 mmol) and 5 ml of glacial acetic acid in absolute ethanol (100 ml) was heated in a water bath with stirring for 18 h at 60–70°C. After cooling the mixture to room temperature the solvent was evaporated and the residue was separated by silica gel chromatography using 5–8% EtOAc in hexanes as eluent to afford compound **9** as an orange yellow solid (2.84 g,

32% yield), m.p. 81–83°C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2 (t, 3H,  $\text{CH}_2\text{--CH}_3$ ), 1.59 (d, 3H,  $\text{CH--CH}_3$ ), 4.15 (q, 2H,  $\text{CH}_2\text{--CH}_3$ ), 5.3 (q, 1H,  $\text{CH--CH}_3$ ), 7.58 (d, 2H, ArH), 7.7 (d, 2H, ArH), 7.85 (d, 2H, ArH), 8.12 (d, 2H, ArH).

#### 2.5. 4-[*(S)*-1-(Ethoxycarbonyl)jethyl

#### 4-[4'-(9-decenyloxy)biphenyl]azobenzoate (**10**)

A 100 ml three-necked flask equipped with condenser, magnetic stirrer and nitrogen inlet was charged with compound **9** (0.607 g, 1.5 mmol), 5 mg of  $\text{Pd}(\text{Ph}_3\text{P})_4$  and 15 ml of toluene. After stirring for 10 min, compound **4** was added immediately followed by 5 ml of 1M  $\text{NaHCO}_3$  solution. The reaction mixture was heated under reflux for 18 h with vigorous stirring. After cooling to room temperature, water (50 ml) and  $\text{CH}_2\text{Cl}_2$  (60 ml) were added to the mixture. The organic layer was separated and washed with saturated NaCl, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. The residue was purified by silica gel chromatography using 3–5% EtOAc in hexanes as eluent to afford compound **10** as an orange yellow solid (0.615 g, 74% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.1–2.1 (m, 20H ( $\text{CH}_2$ ),  $\text{CH}_2\text{--CH}_3$ ,  $\text{CH--CH}_3$ ), 4.02 (t, 2H,  $\text{CH}_2\text{O}$ ), 4.22 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.98 (m, 2H,  $\text{CH=CH}_2$ ), 5.32 (q, 1H,  $\text{CH--CH}_3$ ), 5.8 (m, 1H,  $\text{CH=CH}_2$ ), 7.0 (d, 2H, ArH), 7.60 (d, 2H, ArH), 7.72 (d, 2H, ArH), 7.97 (dd, 4H, ArH), 8.21 (d, 2H, ArH). Anal. calcd for  $\text{C}_{34}\text{H}_{40}\text{O}_5\text{N}_2$ : C 73.38, H 7.19, N 5.04; found: C 73.61, H 7.30, N 5.00%.

#### 2.6. (*S*)-1-(Ethoxycarbonyl)ethyl 4-hydroxybenzoate (**13**)

Thionyl chloride (3.65 ml, 50 mmol) was added slowly to a mixture of 4-hydroxybenzoic acid, **11**, (6.90 g, 50 mmol) and (*S*)-ethyl-lactate (6.24 ml, 55 mmol) in dry acetonitrile (200 ml) cooled on an ice-bath under  $\text{N}_2$ . The resulting mixture was stirred at 0–5°C for 1 h, and then at 35–40°C for 20 h. The mixture was evaporated, and the residue redissolved in  $\text{CH}_2\text{Cl}_2$ , and washed with water. The organic layer was collected, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. The residue was purified by silica gel column chromatography using 0–2%  $\text{CH}_3\text{OH}$  in  $\text{CH}_2\text{Cl}_2$  as eluent to afford a light yellow oil, **13** (7.328 g, 62%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.27 (t, 3H,  $\text{CH}_2\text{--CH}_3$ ), 1.60 (d, 3H,  $\text{CH--CH}_3$ ), 4.24 (q, 2H,  $\text{CH}_2\text{--CH}_3$ ), 5.27 (q, 1H,  $\text{CH--CH}_3$ ), 6.78 (d, 2 aromatic H), 7.86 (d, 2 aromatic H).

#### 2.7. Ethyl 4'-(9-decenyloxy)biphenyl-4-carboxylate (**15**)

Ethyl 4'-hydroxybiphenylcarboxylate, **14** [**16**] (9.20 g, 38 mmol), 9-decen-1-ol, **2** (7.12 ml, 39.9 mmol), and DEAD (6.27 ml, 39.9 mmol) were dissolved in dry THF (60 ml) under nitrogen. The resulting solution was cooled to 0°C while stirring. A solution of triphenylphosphine (9.97 g, 38 mmol) in dry THF (30 ml) was added dropwise to the cooled solution over approximately 20 min,

and the resulting solution allowed to warm to room temperature. Stirring was continued for a further 24 h. The solution was evaporated to dryness and the residue crystallized twice from  $\text{CH}_3\text{OH}$  to afford white crystals of compound **15** (12.0 g, 83% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2–2.1 (m, 17H ( $\text{CH}_2$ ),  $\text{CH}_2\text{--CH}_3$ ), 3.97 (t, 2H,  $\text{CH}_2\text{O}$ ), 4.38 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.95 (m, 2H,  $\text{CH=CH}_2$ ), 5.80 (m, 1H,  $\text{CH=CH}_2$ ), 6.98 (d, 2H, ArH), 7.57 (dd, 4H, ArH), 8.07 (d, 2H, ArH).

#### 2.8. 4'-(9-Decenyloxy)biphenyl-4-carboxylic acid (**16**)

A mixture of **15** (10.30 g, 27.1 mmol), ethanol (80 ml), and KOH (4.54 g, 81.3 mmol) in 20 ml  $\text{H}_2\text{O}$  was heated under reflux for 3 h. The reaction mixture was then cooled, and the precipitate filtered off. The product was added to a mixture of AcOH (80 ml) and ethanol (80 ml), and the mixture stirred for 1 h at 120°C. The reaction mixture was then cooled, and the precipitate filtered off. The final product compound **16**, a white crystalline powder, was obtained by recrystallization from acetic acid/ethanol (80 ml/80 ml), yield 9.20 g, 96%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2–2.1 (m, 14H,  $\text{CH}_2$ ), 3.96 (t, 2H,  $\text{CH}_2\text{O}$ ), 4.95 (m, 2H,  $\text{CH=CH}_2$ ), 5.80 (m, 1H,  $\text{CH=CH}_2$ ), 6.98 (d, 2H, ArH), 7.62 (dd, 4H, ArH), 8.02 (d, 2H, ArH).

#### 2.9. 4-[*(S)*-1-(Ethoxycarbonyl)jethyl

#### {[4'-(9-decenyloxy)j]biphenyl-4-yl}- carbonyloxybenzoate (**17**)

A solution of dicyclohexylcarbodiimide (3.58 g, 17.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) was added to a 250 ml flask containing a solution of **16** (5.02 g, 14.26 mmol), **13** (3.39 g, 14.26 mmol), and 4-(dimethylamino)pyridine (0.18 g, 0.14 mmol) in 100 ml dry  $\text{CH}_2\text{Cl}_2$ . The mixture was heated under reflux for 16 h with stirring; it was then filtered and the filtrate concentrated. The residue was crystallized from ethanol twice and then from hexane to afford white crystals of compound **17** (5.85 g, 72%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2–2.1 (m, 20H ( $\text{CH}_2$ ),  $\text{CH}_2\text{--CH}_3$ ,  $\text{CH--CH}_3$ ), 4.02 (t, 2H,  $\text{CH}_2\text{O}$ ), 4.25 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.96 (m, 2H,  $\text{CH=CH}_2$ ), 5.34 (q, 1H,  $\text{CH--CH}_3$ ), 5.82 (m, 1H,  $\text{CH=CH}_2$ ), 6.98 (d, 2H, ArH), 7.32 (d, 2H, ArH), 7.58 (d, 2H, ArH), 7.67 (d, 2H, ArH), 8.15 (dd, 4H, ArH). Anal. calcd for  $\text{C}_{35}\text{H}_{40}\text{O}_7$ : C 73.43, H 6.99; found: C 73.25, H 7.02%.

#### 2.10. Synthesis of side chain ferroelectric liquid crystalline polymers

To a solution of poly[(30–35 mol %)methylhydro-siloxane-co-(65–70 mol %)dimethylsiloxane] (1.5 mmol of Si–H function) dissolved in 100 ml of dry toluene was added compound **17** (1.115 g, 1.95 mmol). The reaction mixture was heated to 110°C under  $\text{N}_2$  and 45  $\mu\text{l}$  of dicyclopentadienyl platinum (II) chloride solution (1  $\text{mg ml}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) was then injected. The mixture

was heated under reflux under nitrogen for 48 h. The polymer **18b** was obtained by precipitation from methanol twice and dried under vacuum overnight at 100°C. Due to the reprecipitation procedure, some of the lower molecular weight fractions of the copolymer were lost, producing an apparent yield of 63%. NMR showed that more than 98% of the Si–H ( $\delta = 4.74$  ppm, CDCl<sub>3</sub>) bonds had been converted to Si–(mesogenic group) bonds for copolymers and more than 95% for terpolymers.

The above description of the synthesis of polymer **18b** typifies the procedure employed for all polymers described here. For terpolymers **18c** and **18d**, suitable mixtures of compounds **10** and **17** were used.

### 3. Results and discussion

#### 3.1. Synthesis of the azo compound **10**

The synthetic route for compound **10** is shown in schemes 1–3. 4-Bromophenol was reacted with 9-decen-1-ol using dimethyl azodicarboxylate (DEAD) and triphenylphosphine (PPh<sub>3</sub>) to form the alkene phenyl ether **3**. The corresponding Grignard reagent was treated with trimethyl borate to form a dimethyl borate ester which was hydrolyzed to give the boronic acid **4**. 4-Nitrobenzoyl chloride **5** was reacted with (*S*)-ethyl lactate **6** using pyridine as solvent to form the nitrobenzoate derivative **7**. Reaction of **7** with zinc dust followed by oxidation with ferric chloride gave the nitroso compound **8** which was reacted with *p*-bromoaniline under acid conditions to give the azobenzene derivative **9**. Compound **10** was obtained by reaction of **9** with **4** using the standard Suzuki coupling procedure [17].

#### 3.2. Synthesis of the ester compound **17**

Compound **17** was synthesized according to the procedure outlined in schemes 4 and 5. 4-Hydroxybenzoic acid was converted to compound **13** in good yield by reaction with **12** directly without protection of the hydroxyl group. 4'-(9-Decenyloxy)biphenyl-4-carboxylic acid **16** was prepared by reacting ethyl 4'-hydroxybiphenyl-4-carboxylate **14** [16] with 9-decen-1-ol in the presence of DEAD and PPh<sub>3</sub>, followed by hydrolysis. The final product **17** was obtained by esterification of the carboxylic acid derivative **16** with **13** in the presence of dicyclohexyl carbodiimide (DDC) and 4-*N,N*-dimethylamino pyridine (DMAP).

#### 3.3. Polymer synthesis

The polymers **18a–d** were synthesized via the classical hydrosilylation reaction [18] between poly-[(30–35 mol %)methylhydrosiloxane-co-(65–70 mol %)-dimethylsiloxane] and the vinyl mesogenic side groups

**10** and **17** in different ratios (see scheme 6). They were purified by several reprecipitations from methylene chloride into methanol. Their molecular weights were determined by GPC and are given in table 1.

#### 3.4. Phase characterization

The UV-vis spectra recorded in chloroform solutions for all monomers and copolymers consist of two main absorbance bands due to the two different chromophores. The ester group absorbs at 308 nm and the azo group has a broader absorbance with a maximum at 378 nm. The absorption wavelength does not change for any of the structures studied, but it is important to mention that the azo absorbance shows significant tailing at and even beyond 500 nm, which would allow the use of lasers in the visible range to photoinduce isomerization and reorientation.

The transition temperatures and the phases exhibited by the monomers (**10** and **17**), their corresponding copolymers (**18a** and **18b**) and terpolymers (**18c** and **18d**) were determined using a combination of DSC and polarized optical microscopy. The results are summarized in table 2. All compounds form chiral smectic C phases. The two monomers also form a smectic I or smectic F phase. Figure 1 presents typical textures of the smectic phases of **10** and **17**.

The phase diagram for the mixtures of the vinyl monomers **10** and **17** is given in figure 2. It shows that the transition temperatures of the mixtures vary linearly between those of the two pure components, indicating that the two mesogens are completely miscible in all proportions. The SmC\* phase reaches room temperature as the content of monomer **10** (azo derivative) decreases. Spontaneous polarization (figure 3) and tilt angle (figure 4) values were measured as a function of temperature for the SmC\* phase of compound **10**, which was easier to align in the cell [19].

The phase transition temperatures for the copolymers and terpolymers (figure 5) also show a linear dependence on the relative ratios of the two types of mesogenic groups (**10/17**) attached to the polysiloxane backbone, and the temperature range of liquid crystal phases is

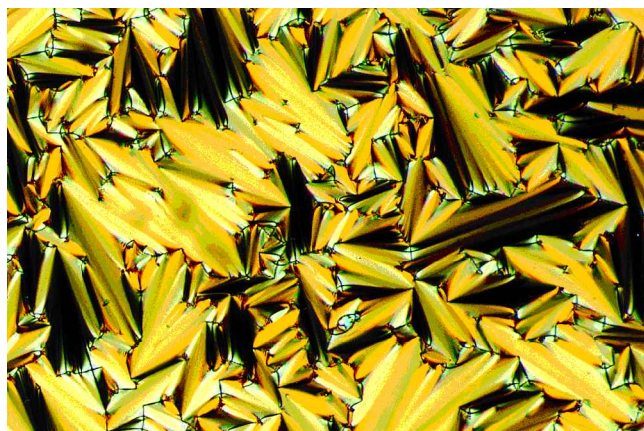
Table 1. Synthesis and properties of polymers

Polymer	Apparent yield/%	$M_n^a$	$M_w^a$	$PD^b$
<b>18a</b>	65	10800	16000	1.48
<b>18b</b>	63	15600	23400	1.50
<b>18c</b>	66	3270	5580	1.70
<b>18d</b>	75	6210	12900	2.10

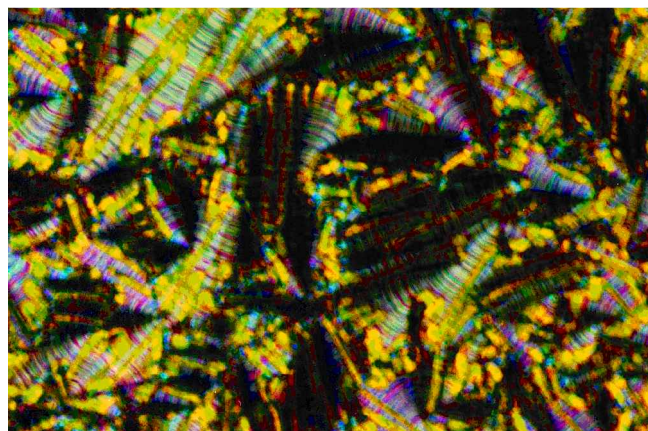
<sup>a</sup> Number- and weight-average molecular weights estimated by GPC.

<sup>b</sup> Polydispersity ( $M_w/M_n$ ).

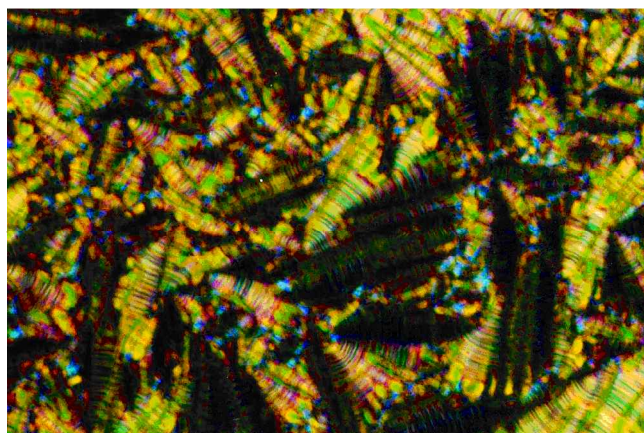




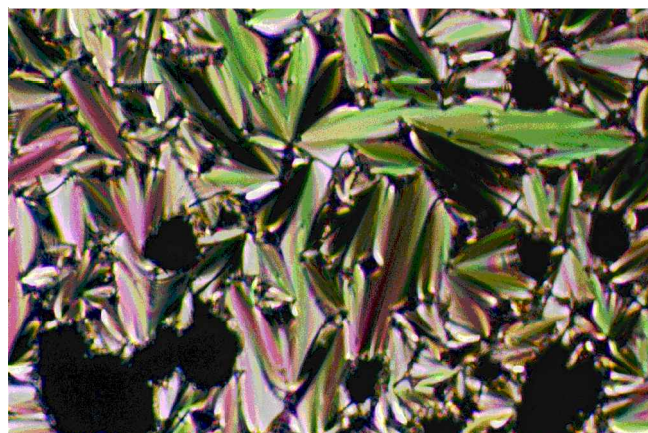
(a)



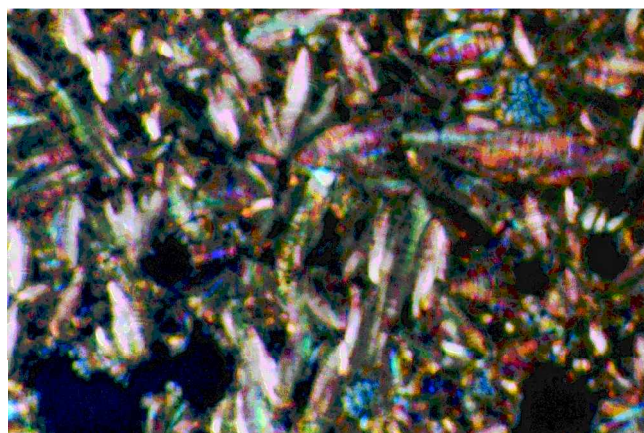
(b)



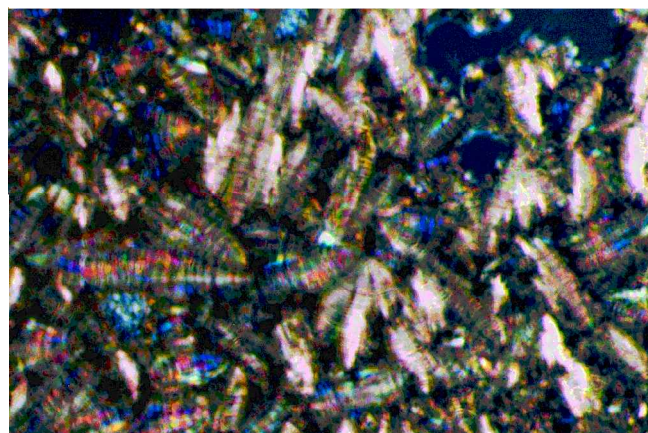
(c)



(d)



(e)



(f)

Figure 1. Textures observed under polarized light microscopy for the azo compound **10** at 166°C (SmA) (a), 100°C (SmC\*) (b) and 60°C (SmI or F) (c); also for the ester compound **17** at 148°C (SmA) (d), 110°C (SmC\*) (e) and 30°C (SmI or F) (f).

dramatically decreased as the azo content is increased. The copolymer **18b** derived from the ester monomer **17** exhibits an Isotropic  $\rightarrow$  SmA\*  $\rightarrow$  SmC\* phase sequence with decreasing temperature, and forms a SmC\* phase at room temperature. But the copolymer **18a** derived

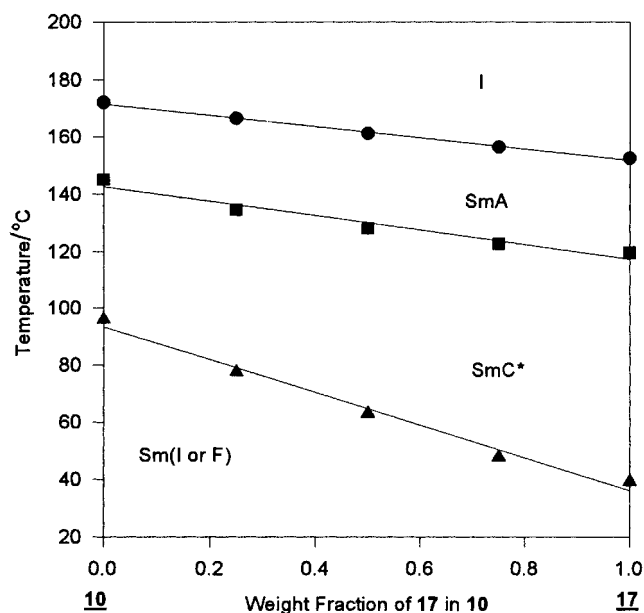
from azo monomer **10** shows no liquid crystalline phase at all; it is an amorphous polymer. However, the terpolymers with small azo contents do form SmC\* phases at room temperature and they could be suitable for photoswitching studies.



Table 2. Phase and transition temperatures determined from a combination of optical microscopy, DSC, and spontaneous polarization measurement techniques.

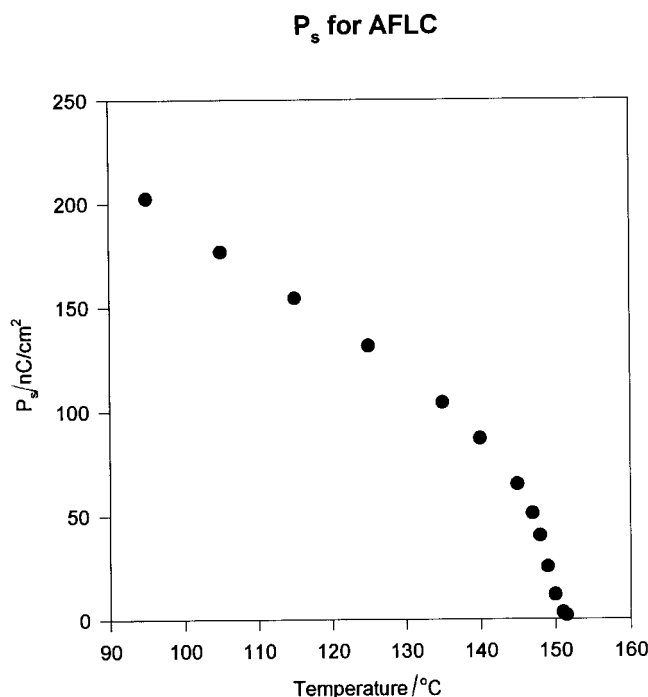
Material	Phase sequence/ $^{\circ}\text{C}$
Monomer <b>10</b>	Cr 38.6 Sm(I or F) 96 SmC* 145 SmA 172 I
Monomer <b>17</b>	Cr 4.5 Sm(I or F) 39.2 SmC* 119.6 SmA 152.4 I
Mixture 1 (75% <b>10</b> + 25% <b>17</b> )	Cr 20.3 Sm(I or F) 77.5 SmC* 134.5 SmA 166.4 I
Mixture 2 (50% <b>10</b> + 50% <b>17</b> )	Cr 6.6 Sm(I or F) 63 SmC* 128 SmA 161.1 I
Mixture 3 (25% <b>10</b> + 75% <b>17</b> )	Cr - 1.4 Sm(I or F) 47.8 SmC* 122.7 SmA 156.4 I
Copolymer <b>18a</b> (from <b>10</b> )	<sup>a</sup> Amorphous
Copolymer <b>18b</b> (from <b>17</b> )	<sup>a</sup> $T_g$ SmC* 152.8 SmA 179 I
Terpolymer <b>18c</b> (4.2% azo mesogen)	<sup>a</sup> $T_g$ SmC* 145 SmA 165 I
Terpolymer <b>18d</b> (25.1% azo mesogen)	<sup>a</sup> $T_g$ SmC* 102 SmA 137 I

<sup>a</sup> The glass transition was not visible in the DSC scans, its expected range should be around  $0^{\circ}\text{C}$ , in comparison with similar copolymers and terpolymers [13].

Figure 2. Phase diagram for mixtures of the mesogenic side groups **10** and **17**.

#### 4. Conclusion

The synthesis and characterization of two new ferroelectric liquid crystals (biphenyl azobenzene derivative **10** and phenyl biphenyl carboxylate derivative **17**) are described. New side-chain polysiloxane copolymers (**18a** and **18b**) and terpolymers (**18c** and **18d**) were synthesized by reacting poly[(30–35 mol %)methylhydrosiloxane-co-(65–70 mol %)dimethylsiloxane] with the mesogenic side groups **10** and **17**. Their properties were also

Figure 3. Spontaneous polarization of **10** as a function of temperature in the SmC\* phase.

characterized. Both **10** and **17** form Isotropic, SmA\*, SmC\*, and Sm(I or F)\* phase sequences. The transition temperatures of **10/17** mixtures vary linearly between those of the two pure components. The phase behaviour of the side chain polysiloxanes is markedly influenced by their azo content. A high azo mesogenic group content of the polymers produced amorphous terpolymers. Terpolymers with low azo content exhibited a SmC\* phase at room temperature. They are suitable to be

## Tilt angle for AFLC

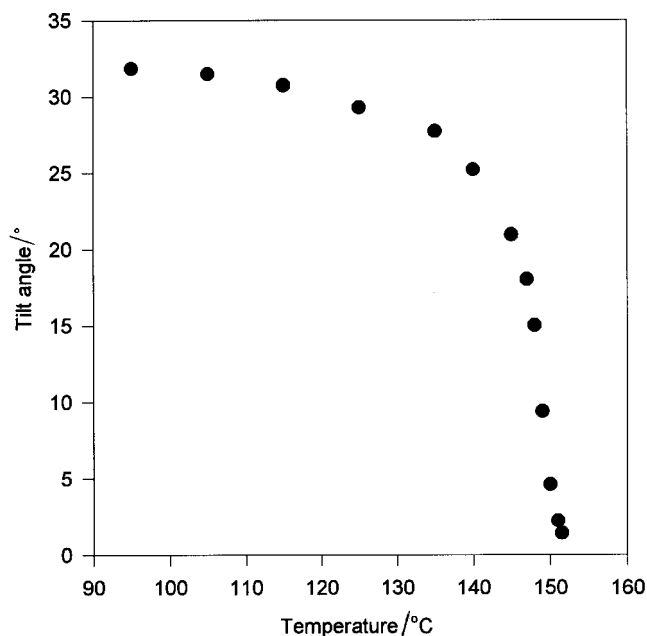


Figure 4. Tilt angle of **10** as a function of temperature in the SmC\* phase.

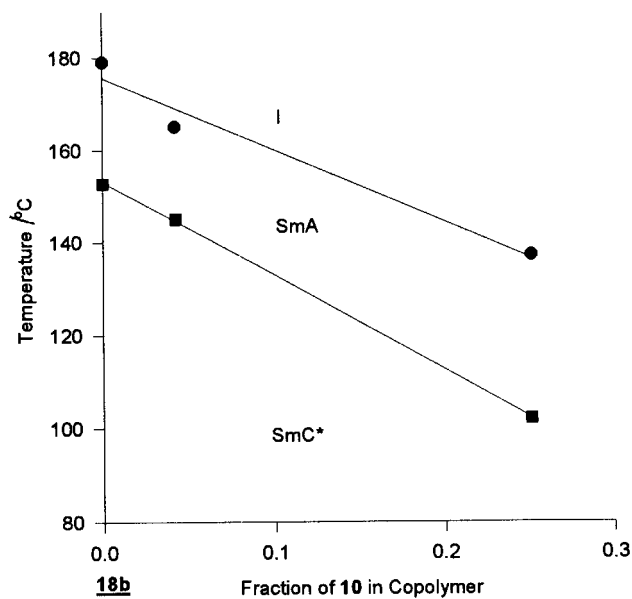


Figure 5. Phase diagram of the copolymers.

used for isomerization, orientation and photoswitching studies currently in progress.

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