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Synthesis and evaluation of a series of novel 2-substituted poly(allylalcohol) side chain liquid crystalline oligomers exhibiting ferroelectricity

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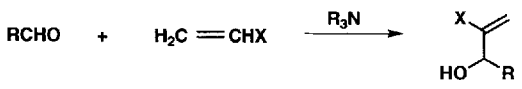
The recently published Baylis–Hillman methodology has been used to prepare a number of side chain liquid crystalline poly(allylalcohols) incorporating a ferroelectric mesogenic side chain. These poly(allylalcohols) exhibited wide range S_C^* phases and, in the case of two of these materials, low glass transition temperatures. The transition temperatures and phase behaviour of the SCLC poly(allylalcohols) were compared to acrylate and methacrylate SCLC oligomers containing a similar mesogenic side chain. The response times for two poly(allylalcohols) exhibiting low glass transition temperatures were also measured over a wide temperature range. Although the poly(allylalcohols) had comparable response times to the analogous acrylate and methacrylate SCLCP, they showed the greater temperature dependence of the response time. However, at 39°C one of the SCLC poly(allylalcohols) showed a response time of 65 ms.

1. Introduction

In a recent paper [1], we described the preparation and thermal properties of a series of side chain liquid crystalline oligomers which were derived from the Baylis–Hillman reaction [2], a procedure which places polar functional groups along the polymeric backbone (scheme 1). The object of that work was to examine the mesogenic properties of these oligomers using simple cyanobiphenylyl mesogenic side groups. We also speculated on the macrostructure of the backbones of these novel poly(allylalcohols), in particular on the influence of the lateral hydroxyl group in controlling tacticity. These oligomers displayed either nematic or smectic A phases.



R=mesogenic group
X=CN, $COCH_3$ or CO_2CH_3

Scheme 1. The Baylis–Hillman reaction.

In the work presented in this paper similar polymer backbones to those mentioned in our previous paper [1] were employed, but in this work, we have used these backbones in conjunction with a mesogenic side group which is known to promote smectic C* phases when used in other polymeric systems [3]. The object of the present work was to see if these unique polymeric architectures incorporating a ferroelectric mesogenic side group would (i) form ferroelectric SCLCP with fast response times, comparable to those shown by other ferroelectric SCLCP, and (ii) exhibit the required combination of liquid crystalline phases to aid good alignment, i.e. the combination of a narrow temperature range smectic A phase or a nematic phase and a wide temperature range smectic C* phase (ferroelectric phase) which should extend ideally below room temperature.

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2. Synthesis

The methods used to prepare the monomers and oligomers are outlined in schemes 2–4.

2.1. *Scheme 2, synthesis of aldehydes 10a and 10b*

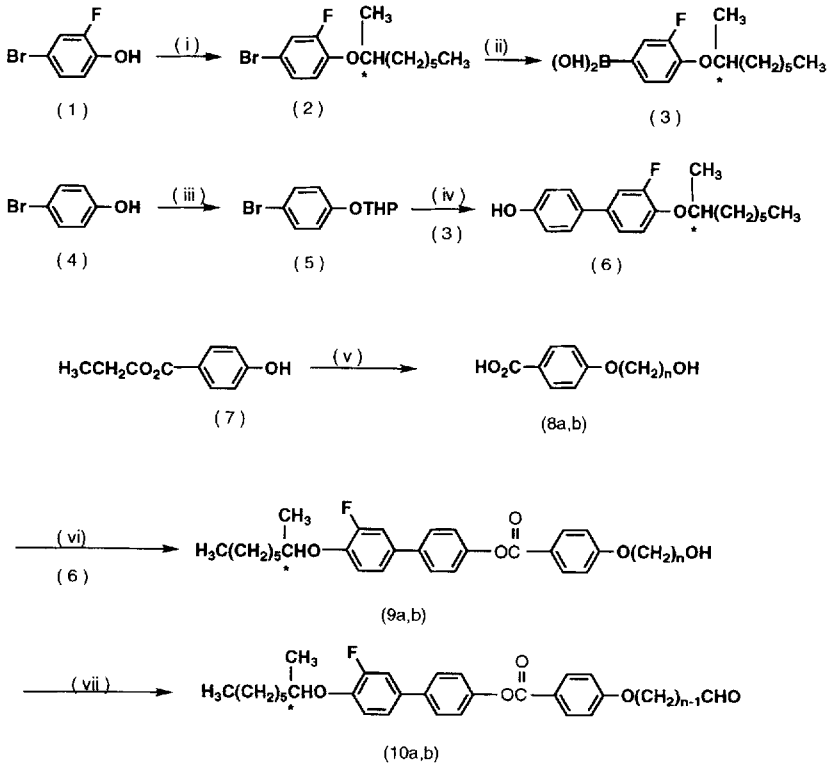
Aldehydes **10a** and **10b**, which include both the spacer group and the mesogenic side group, were derived using the synthetic route shown in scheme 2. 4-Bromo-2-fluorophenol was reacted with (R)-(-)-2-octanol using diethyl azodicarboxylate (DEAD) and triphenylphosphine to form the alkyl phenyl ether **2**. This was then reacted with magnesium followed by trimethyl borate to form a dimethyl borate ester which was hydrolysed without prior isolation of the product to give the boronic acid **3**. 4-Bromophenol was protected with a tetrahydropyranyl group and then reacted with boronic acid **3** using the standard boronic acid coupling procedure [4]. Deprotection of the resultant biphenylyl compound gave hydroxybiphenyl **6** which was reacted with the appropriate acid **8a** or **8b** using dicyclohexylcarbodiimide (DCC) to produce the biphenylyl benzoate alcohol **9a** or **9b**. Oxidation of alcohols **9a** and **9b** with pyridinium dichromate produced aldehydes **10a** and **10b**.

2.2. *Scheme 3, synthesis of monomers 11a–f*

As in previous work [1], the aldehydes **10a** or **10b**, (scheme 2) were reacted with either acrylonitrile, methyl acrylate or methyl vinyl ketone using the tertiary amine 3-quinuclidinol as the catalyst. The reaction rate varied according to the reactivity of the activated alkene. For example, the reaction with methyl acrylate required about 14 days to complete, whilst the reaction with methyl vinyl ketone needed only 36 hours. In this latter case the reaction had to be moderated with tetrahydrofuran [5].

2.3. *Scheme 4, oligomerization of monomers 12a–f*

Monomers **11a–f** were oligomerized by photoinitiation between glass plates using a commercial photoiniti-



8a, **9a**, **10a** ... $n=7$; **8b**, **9b**, **10b** ... $n=11$.

(i) *R*(-)-2-octanol, DEAD, PPh_3, THF
(ii) (a) Mg, $B(OCH_3)_3$, THF; (b) $HCl_{(aq.)}$
(iii) 3,4-dihydro-2H-pyran, p-TSA, dichloromethane
(iv) (a) $Pd(PPh_3)_4$, Na_2CO_3, toluene; (b) p-TSA, dichloromethane
(v) (a) 7-bromoheptan-1-ol or 13-bromoundecan-1-ol, K_2CO_3, butanone; (b) KOH, EtOH, H_2O
(vi) DCC, DMAP, THF
(vii) Pyridinium dichromate, sodium acetate, 4Å molecular sieves, dichloromethane

Scheme 2. Synthetic route to the preparation of aldehydes **10a** and **10b**.

ator [6] and a UVA sunlamp. This method gave DP values in the range 5–10 and polydispersities $<1{\cdot}5$.

3. Results and discussion

3.1. *Characterization study*

The transition temperatures (DSC), phase behaviour (optical microscopy and X-ray diffraction) and gel permeation chromatography (GPC) data for the two series of oligomers synthesized are given in table 1. It has not yet been possible to measure the tilt angles for the S_C phases by X-ray analysis with any accuracy because of alignment problems.

Examination of table 1 shows that the length of the spacer group is crucially important in determining the type of mesophase which is formed by these oligomers. Oligomers with the shorter spacer group ($n = 7$) show either smectic A phases, where $X = CN$ or $COCH_3$ or no phase at all where $X = CO_2CH_3$. Oligomers with the longer spacer group ($n = 11$), however, show smectic C* phases with all three of the backbones employed. The oligomer where $X = COCH_3$ is particularly interesting since the smectic C* phase has a temperature range of 2·5 to 59·0°C, followed by a narrow range nematic phase in the temperature range 59·0 to 69·0°C. The combination of a narrow temperature range nematic phase and a wide temperature range smectic C* phase, which extends below room temperature, fulfils the requirement outlined in § 1 with respect to phase structure and phase temperature range, and therefore this polymer could be a useful material for ferroelectric device applications.

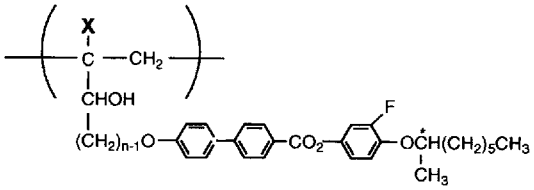
The transition temperatures for the three Baylis–Hillman oligomers were then compared to more commonly known poly(acrylate), poly(methacrylate) and poly(chloroacrylate) materials carrying a similar mesogenic side chain, and the relevant data are given in table 2. The phase behaviour for these systems is best expressed as a bar graph, given in figure 1. It is quite clear from figure 1 that all seven materials exhibit wide S_C^* ranges but in the case of the Baylis–Hillman oligomers (**5**, **6** and **7**), no underlying smectic phase was observed below the S_C^* phase. Indeed, only in the case of oligomer **6** is another phase, other than a S_C^* phase (a chiral nematic phase), exhibited by the Baylis–Hillman materials.

In the case of **5**, the S_C^* range for this oligomer is in the same temperature range as that for the poly(acrylate), poly(methacrylate) and poly(chloroacrylate), but **6** and **7** have S_C^* ranges at much lower temperatures, so much so, that the Baylis–Hillman materials **6** and **7** exhibit room temperature S_C^* phases. Although the Baylis–Hillman oligomers **6** and **7** have slightly lower DP values than the acrylate, methacrylate and chloroacrylate materials, this would not account for the loss of the underlying smectic phase, thus allowing the two Baylis–Hillman materials to exhibit room temperature S_C^* phase. The structure of the backbone for the Baylis–Hillman oligomers must hinder the formation of the more highly ordered smectic phases. This makes oligomers **6** and **7** very exciting materials for ferroelectric display devices and for this reason a response time study was carried out on these two materials.

3.2. *Response time study*

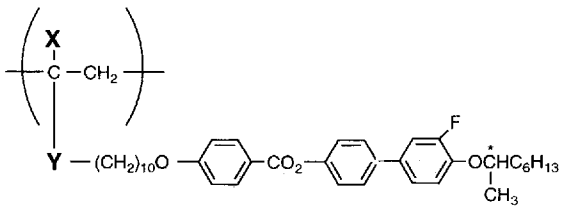
Seven SCLC oligomers were chosen for this study and their structure, DP values and thermal properties are given in table 2. All the SCLC oligomers are structurally similar except for (i) the point of attachment of the spacer and mesogenic side groups onto the backbone (position *Y* in the structure given in table 2), and (ii) the head group which is attached along the length of the

Table 1 The transition temperatures and GPC data for the Baylis–Hillman oligomers.



$X =$	CN	$COCH_3$	CO_2CH_3
$n = 7$	g 77·0 S_A 119·0°C I $M_w = 7950$ $M_n = 5430$ $M_w/M_n = 1{\cdot}5$	g 34·0 S_A 64°C I $M_w = 3710$ $M_n = 3090$ $M_w/M_n = 1{\cdot}2$	g 31·0°C I $M_w = 3220$ $M_n = 2850$ $M_w/M_n = 1{\cdot}1$
$n = 11$	g 74·0 S_C^* 135·0°C I $M_w = 7250$ $M_n = 5240$ $M_w/M_n = 1{\cdot}4$	g 2·5 S_C^* 59·0 N* 69·0°C I $M_w = 4730$ $M_n = 3860$ $M_w/M_n = 1{\cdot}2$	g 18·0 S_C^* 90·0°C I $M_w = 4550$ $M_n = 4030$ $M_w/M_n = 1{\cdot}1$

Table 2. The structure, thermal properties and DP values of SCLC oligomers containing similar ferroelectric mesogenic side groups.



Oligomer	*X*	*Y*	DP	S_C range (°C)	Transition temperatures (°C) g		S		S_I		S_C^*		S_A		N*		I
1	H	CO_2	12	77·3	•	30·6	•	48·7			•	126·0	•	136·9			•
2	H	CO_2CH_2	12–15	81·0	•	28·0			•	53·0	•	134·0	•	147·0			•
3	CH_3	CO_2CH_2	12–15	55·0			•	65·0			•	120·0	•	144·0			•
4	Cl	CO_2CH_2	12–15	79·0			•	51·0			•	130·0	•	142·0			•
5	CN	CHOH	8–10	61·0	•	74·0					•	135·0					•
6	$COCH_3$	CHOH	8–10	56·5	•	2·5					•	59·0			•	69	•
7	CO_2CH_3	CHOH	8–10	72·0	•	18·0					•	90·0					

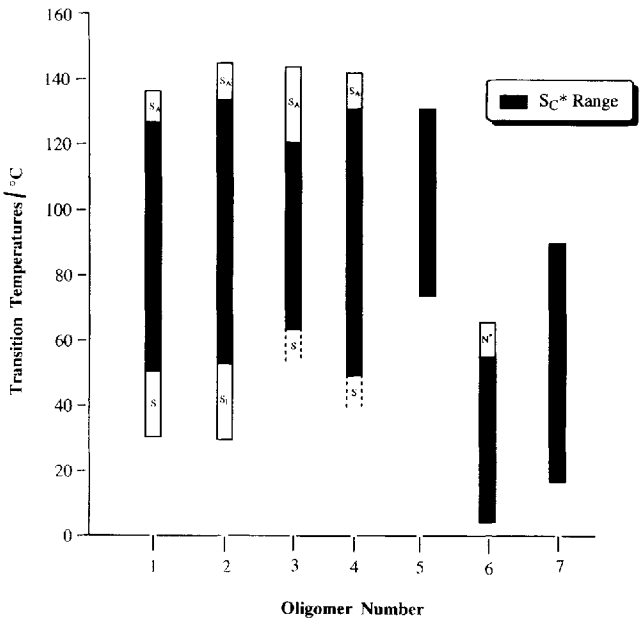


Figure 1. Phase behaviour of SCLC oligomers containing similar ferroelectric mesogenic side groups.

backbone (position *X* in the structure given in table 2). In the case of SCLC oligomers **1** to **4**, these materials were chosen because they contained well established backbones which are used extensively in liquid crystal polymer research. The SCLC oligomers **5** to **7** are the Baylis–Hillman analogues.

Materials were heated into the isotropic phase and flow filled into glass cells. These cells were constructed 'in house' at DRA, Malvern, and consisted of two glass plates with ITO electrodes and a rubbed polyimide layer. The two plates were assembled with the top and bottom plate rubbing directions parallel and using a UV curable adhesive and 2 μm glass spacer beads. The structure of the cell is given in figure 2.

When electrical connections had been made, the cells were mounted in a Mettler hot stage and then placed between crossed polarizers on a Nikon Microphot microscope. The cell was rotated in order to achieve the maximum contrast between the light and dark states. A 1 Hz square wave of 20 V peak to peak amplitude was applied to the cell. A photosensitive resistor mounted on the microscope recorded the change in optical transmittance through the cell. The output from the resistor and the function generator was supplied to a dual channel oscilloscope. This measured the time lag between the application of the square wave from the function generator and the change in optical response of the cell. The results quoted represent the time between application of the leading edge of the square wave and a 90 per cent change in transmittance through the cell.

The response times (ms) over a range of temperatures for the acrylate (**2**) and methacrylate (**3**) SCLC oligomers are given in figure 3. No response times were recorded for the chloroacrylate (4) because the material was thermally unstable. The response times for oligomers **6** and **7** are given in figure 4, but no data were recorded for **5** because the oligomer degraded prior to filling the cell.

For oligomers **3**, **6** and **7** there was a sharp decrease in response time with increase in temperature, but as the temperature approached the upper S_C^* transition (for **2** and **3** the upper transition is the S_C^*–S_A transition, but for **6** this is the S_C^*–N transition and for **7** the S_C^*–I

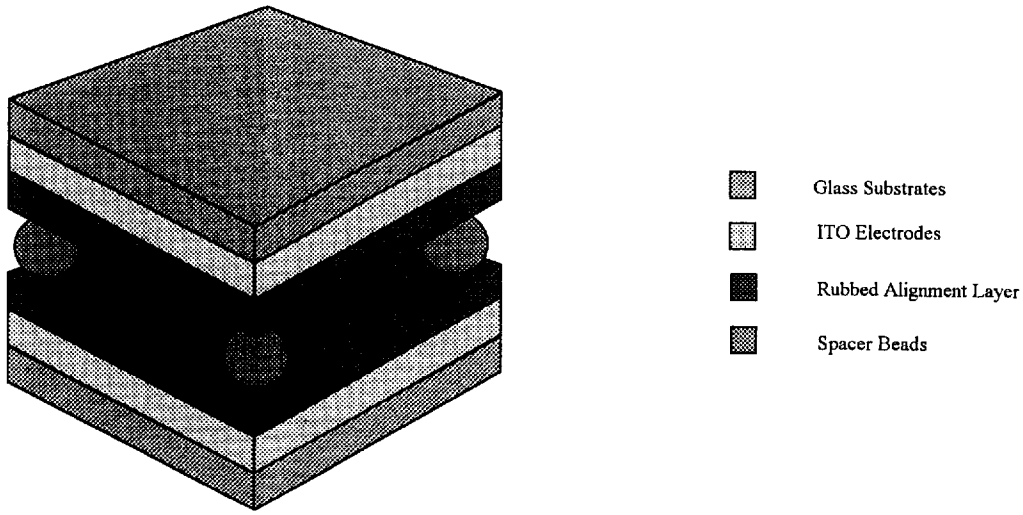


Figure 2. Structure of the cell used to measure response times.

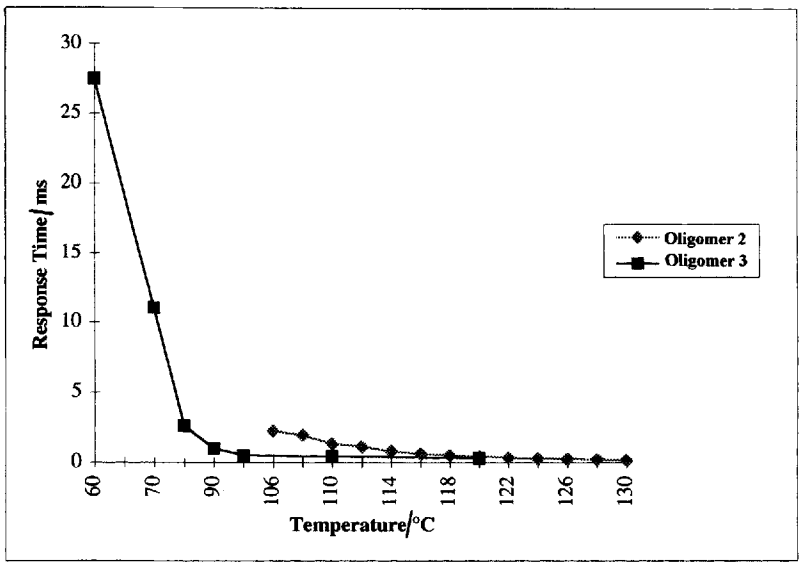


Figure 3. A plot of response time (ms) against temperature (°C) for oligomers 2 and 3.

transition), the response times levelled off to give response times below 1 ms. It is very clear from figures 3 and 4 that the two sets of oligomers, i.e. the acrylate/methacrylate and the Baylis–Hillman materials, are operating in different temperature regimes. To make a more valid comparison of the response times for these oligomers, we have taken the response times at a temperature 20 and 25° below the upper S_C^* transition. The data are given in table 3. These results show that the response times for oligomer **7** are comparable to those for the more commonly used oligomers **2** and **3**, although the increase in response time with decrease in temperature is far greater for **7**, i.e. the Baylis–Hillman oligomer.

In the case of **6**, this has a very long response time (101 ms) at 20° below the upper S_C^* transition and therefore looks, at first sight, to be a very poor candidate for a display device material. However, it must be remembered that the actual temperature at which the response time for this polymer was measured, 39°C, was very close to room temperature and there are very few ferroelectric SCLC polymers which exhibit both a room temperature S_C^* phase and a low glass transition temperature. Indeed, both of the Baylis–Hillman oligomers give wide temperature S_C^* ranges and even at a temperature of 39°C, the response times for polymers **6** and **7** are 101 and 65 ms, respectively.

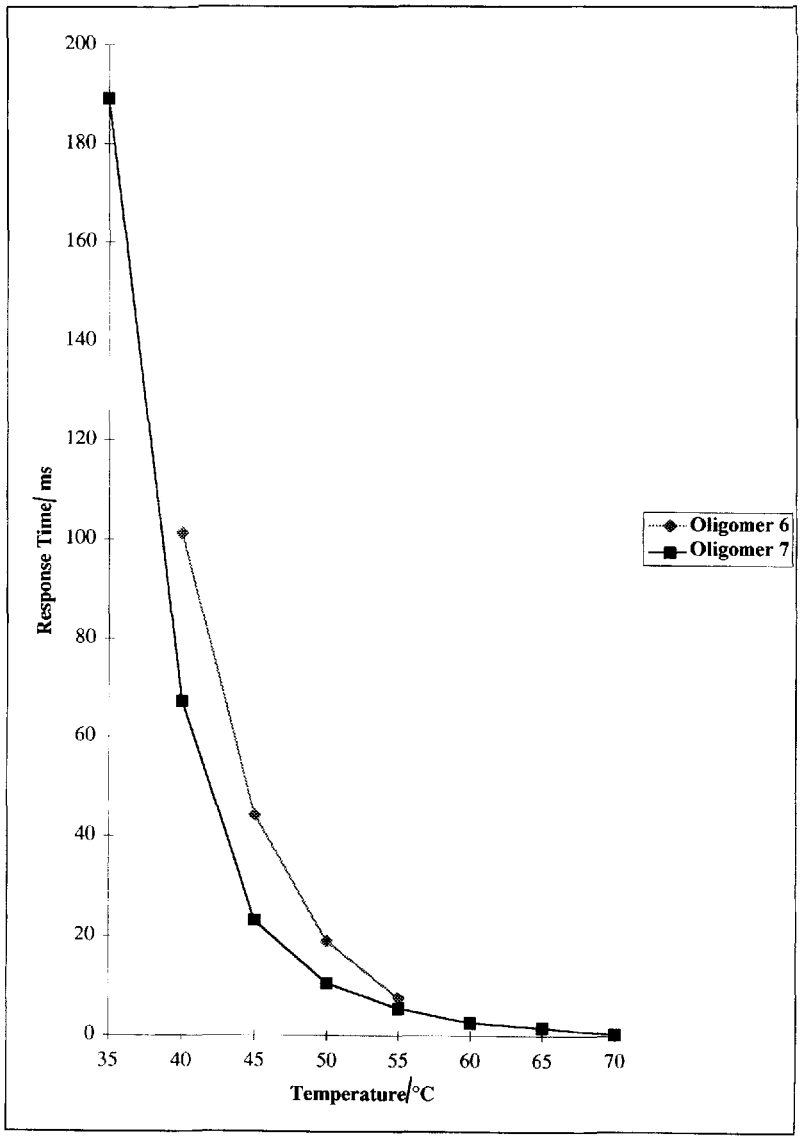


Figure 4. A plot of response time (ms) against temperature (°C) for oligomers 6 and 7.

Table 3. The response times for oligomers 2, 3, 6 and 7 at 20° and 25° below the upper S_C^* transition.

Oligomer	Response times (ms)	
	20° below upper S_C^* transition	25° below upper S_C^* transition
2	0·79 (114)[a]	1·63 (109)
3	0·50 (100)	0·75 (95)
6	101 (39)	—
7	0·33 (70)	1·58 (65)

[a] The figures in brackets are the temperatures at which the response times were measured.

4. Conclusions

The oligomeric materials described in this paper and those previously described [1] show that these 2-substituted poly(allylalcohol) backbones, in combination with appropriate spacer and mesogenic groups, produce interesting side chain liquid crystal materials. In this work, the poly(allylalcohol) backbones were combined with a mesogenic group which is known to promote smectic C* phases when employed with other backbones [2]. For this phase to be formed with the poly(allylalcohol) backbone, the length of the spacer group appears to be of crucial importance. Comparison of the two series of compounds described in this paper, i.e. when $n = 7$ or 11, (see table 1) shows that only the

series with the longer spacer group displays the smectic C* phase. For one member of this series, where $X = COCH_3$, the smectic C* phase has a temperature range which extends from 59°C to below room temperature. This may be a useful compound for ferroelectric display device application since the smectic C* is accompanied by a narrow range chiral nematic phase which should aid alignment. None of the polymers with the shorter spacer chain ($n = 7$) exhibited smectic C* phases.

The response time study showed that both Baylis–Hillman oligomers had comparable response times to a comparable acrylate and a methacrylate carrying the same mesogenic side group, although the increase in response time with decrease in temperature was far greater for the Baylis–Hillman oligomers. At a temperature of 39°C, oligomers **6** ($X = COCH_3$) and **7** ($X = CO_2CH_3$) had response times of 101 and 65 ms, respectively.

5. Experimental

5.1. *Chemical characterization*

The structures of the intermediates, monomers and oligomers were confirmed by one or more of the following techniques: ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (JEOL JNM-GX 270 MHz spectrometer), infrared spectroscopy (Perkin-Elmer 783 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020G/MS spectrometer). The phase transition temperatures were measured using a Mettler FP 52 hot-stage and a FP 5 control unit in conjunction with an Olympus BH2 polarizing microscope, and these results were confirmed by using differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7C, with data station and cooling accessory). The instrumental accuracy of the calorimeter was calibrated against an indium standard. Glass transition temperatures of the SCLC oligomers were measured using the DSC-7C calorimeter. Purities of the intermediates and monomers were checked by NMR spectroscopy (JEOL JNM-GX 270 MHz spectrophotometer), thin layer chromatography (silica gel, single spot purity) and reverse phase HPLC chromatography (5 μm pore size 25 × 0·46 cm ODS Microsorb Dynamax column, eluting with methanol or acetonitrile, >99 per cent). Polydispersities (M_w/M_n) and degrees of polymerisation were determined by gel permeation chromatography (GPC) using a PLgel column (5 μm, 30 × 0·75 cm mixed C column) as the stationary phase and tetrahydrofuran as the mobile phase. The column was calibrated using polystyrene standards ($M_p = 1000$–$430\,500$). Identification of the mesophases was carried out by optical microscopy and X-ray diffraction (using the facilities at the University of Bristol). Specific optical rotations were determined in the temperature range 22–24°C using an Optical Activity type AA10 polarimeter.

5.2. *Scheme 2*

The process described in scheme 2 was used to synthesize the following compounds.

5.2.1. *(S)-(2-Octyl)oxy-4-bromo-2-fluorobenzene (2)*

4-Bromo-2-fluorophenol (52 mmol), (R)-(-)-2-octanol and diethyl azodicarboxylate (DEAD) (53 mmol) were dissolved in dry tetrahydrofuran (75 cm^3) under dry nitrogen and the resultant solution was cooled to 0°C whilst stirring. A solution of triphenylphosphine (52 mmol) in dry tetrahydrofuran (36 cm^3) was added dropwise to the cooled solution over approximately 30 min. and the resultant solution was allowed to rise to room temperature. Stirring was continued for a further 48 h. The tetrahydrofuran was then removed *in vacuo* and the residue redissolved in dichloromethane (150 cm^3). The solution was washed with water (2 × 100 cm^3) and dried ($MgSO_4$). Purification using flash chromatography on silica gel, eluting with a mixture of dichloromethane: petroleum fraction (b.p. 40–60°C) (3:1) gave compound **2** as a clear oil (yield = 85 per cent).

M.s. *m/z*: 302, 304 (M^+), 189, 191. IR (KCl) cm^{-1}: 2950, 2915, 2860, 1600, 1580, 1490, 1300, 1265, 1130, 855. ^1H NMR. ($CDCl_3$) δ: 0·80–0·90 (m, 3H), 1·20–1·85 (m, 13H), 4·30 (sextet, 1H), 6·75 (m, 1H), 7·10–7·30 (m, 2H).

5.2.2. *4-[(S)-2-Octyl]oxy-3-fluorophenyl boronic acid (3)*

Magnesium (31 mmol) in dry tetrahydrofuran (1·0 cm^3) was stirred under dry nitrogen at room temperature. (*S*)-(2-Octyl)oxy-4-bromo-2-fluorobenzene **2** (23 mmol) was dissolved in dry tetrahydrofuran (10 cm^3) and a few drops of this solution was added to the magnesium/tetrahydrofuran mixture. A crystal of iodine was added and the mixture warmed to a gentle reflux. Once the iodine colour was discharged, the heat was removed and the remaining bromophenyl compound in tetrahydrofuran was added dropwise to achieve a continuous self-sustaining reflux of the reaction mixture. When addition was complete, reflux was continued for a further 2 h. The reaction mixture was then cooled to 0–5°C and trimethylborate (31 mmol) in dry tetrahydrofuran (2 cm^3) was added slowly with stirring. The mixture was stirred for a further 30 min at 0–5°C. Dilute hydrochloric acid (20 per cent v/v, 10 cm^3) was added carefully and the mixture was stirred for 15 min at room temperature. The product was extracted into diethyl ether (50 cm^3) and the solution shaken with water (2 × 50 cm^3) and finally dried ($MgSO_4$). Removal of solvent left compound **3** as a thick yellow oil which was

used without purification in the next step (yield = 89 per cent).

M.s. *m/z*: 268 (M^+), 251, (M-17), 124. IR (KCl) cm^{-1}: 2960, 2920, 2860, 1605, 1505, 1420, 1340 (B–OH), 1320, 1270, 740.

5.2.3. *1-Bromo-4-(tetrahydropyranyloxy)benzene (5)*

3,4-Dihydro-2H-pyran (51 mmol) was added dropwise over 10 min. to a stirred, cooled (0°C) solution of 4-bromophenol (41 mmol) in dry dichloromethane (30 cm^3). After the addition was complete, two small crystals of 4-toluenesulphonic acid were added which effected an immediate rise in reaction temperature. After 10 min the reaction mixture was quenched by addition of solid sodium hydrogen carbonate. Removal of the solvent *in vacuo* left a white waxy solid which was redissolved in ethyl acetate and passed through a short silica gel column, eluting with dichloromethane. Removal of the solvent *in vacuo* followed by recrystallization from hexane gave compound **5** as a white waxy solid (yield = 97 per cent), m.p. 51–53°C.

M.s. *m/z*: 256, 258 (M^+), 172, 174.

IR (KCl) cm^{-1}: 2970, 2940, 2870, 1585, 1480, 1235, 1200, 1175, 1120, 1020, 955, 915, 820. ^1H NMR. δ: ($CDCl_3$) 1·50–1·65 (m, 4H), 1·85–2·10 (m, 2H), 3·60 (m, 1H), 3·85 (m, 1H), 5·40 (t, 1H), 6·85 (d, 2H), 7·55 (d, 2H).

5.2.4. *3-Fluoro-4-[(S)-2-octyloxy]-4'-hydroxybiphenyl (6)*

1-Bromo-4-(tetrahydropyranyloxy)benzene (18 mmol) was dissolved in dry toluene (40 cm^3) with stirring and under dry nitrogen. Tetrakis(triphenylphosphine) palladium(0) (0·05 g) was added, followed by sodium carbonate solution (2M) (20 cm^3) and 4-[(S)-2-octyl]oxy-3-fluorophenylboronic acid (**3**) in ethanol (10 cm^3), and the mixture refluxed for 24 h. The mixture was then cooled and water (100 cm^3) added followed by toluene (100 cm^3). The organic phase was separated and washed with water (2 × 50 cm^3), then dried ($MgSO_4$). Removal of the solvent *in vacuo* left a dark coloured oil. The oil was dissolved in dichloromethane and 4-toluenesulphonic acid (0·5 g) was added in one portion. The mixture was stirred for 90 min. and then the solvent removed *in vacuo* to leave a dark coloured solid. Purification using flash chromatography on silica gel, eluting first with dichloromethane followed by diethyl ether gave compound **6** as a pink waxy solid (yield = 69 per cent), m.p. 46–48°C.

M.s. *m/z*: 316 (M^+), 204. IR (KCl) cm^{-1}: 3600–3200, 2960, 2920, 2860, 1610, 1590, 1500, 1450, 1375, 1260, 1240, 1130, 830, 805. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·20–1·65 (m, 12H), 1·70–1·85 (m, 1H), 4·35 (sextet, 1H), 4·85 (s, 1H), 6·85 (d, 2H), 7·00 (t, 1H), 7·15–7·35 (m, 2H), 7·40 (d, 2H).

5.2.5. *7-(4-Carboxy-1-oxyphenyl)heptan-1-ol (8a)*

A mixture of ethyl 4-hydroxybenzoate (60 mmol), 7-bromo-1-heptanol (60 mmol) and potassium carbonate (0·18 mol) in dry butanone (100 cm^3) was boiled for 24 h. Excess of potassium carbonate was separated by filtration and the solvent removed *in vacuo* to leave a white solid. The solid was then dissolved in a water:ethanol mixture (200 cm^3) (1:5). Potassium hydroxide (3·0 g) was added and the mixture heated under reflux for 4 h. The resultant solution was then cooled and acidified to pH 1·0 (universal indicator paper) using hydrochloric acid (6M). Solvents were removed *in vacuo* and the white residue recrystallized from aqueous acetone to leave compound **8a** as a white powder (yield = 84 per cent), m.p. 148–150°C.

M.s. *m/z*: 252 (M^+), 234, 138. IR (KCl) cm^{-1}: 3650 3160, 2920, 2860, 2670, 2555, 1670, 1600, 1570, 1430, 1300, 1115, 840. ^1H NMR (DMSO) δ: 1·25–1·55 (m, 9H), 1·80 (quin., 2H), 3·55 (t, 2H), 4·05 (t, 2H), 6·90 (d, 2H), 8·0 (d, 2H).

5.2.6. *11-(4-Carboxy-1-oxyphenyl)undecan-1-ol (8b)*

This compound was prepared by a procedure analogous to that used for compound **8a**. Yield = 85 per cent, m.p. 142–144°C.

M.s. *m/z*: 308 (M^+), 290, 138. IR (KCl) cm^{-1}: 3700–3200, 2920, 2860, 2670, 2560, 1670, 1600, 1575, 1430, 1300, 1250, 1115, 840, 770. ^1H NMR (DMSO) δ: 1·20–1·60 (m, 17H), 1·80 (quin., 2H), 3·55 (t, 2H), 4·05 (t, 2H), 6·90 (d, 2H), 8·00 (d, 2H).

5.2.7. *7-[1-(Oxy)-4-(4'-(S)-(-)-2-octyloxy-3'-fluorobiphenylyl)carboxyphenyl]heptan-1-ol (9a)*

A mixture of 3-fluoro-4-[(S)-2-octyloxy]-4'-hydroxybiphenyl (**6**) (9·50 mmol), 7-(4-carboxy-1-oxyphenyl)heptan-1-ol (**8**) (10·0 mmol), dicyclohexylcarbodiimide (DCC) (10 mmol) and 4-dimethylaminopyridine (DMAP) (0·125 g) in dry tetrahydrofuran (100 cm^3) was stirred for 3·5 h. The mixture was then filtered and the solvent removed *in vacuo* to leave a white solid. Purification of the solid using flash chromatography on silica gel eluting with a mixture of ethyl acetate:petroleum fraction (b.p. 40–60°C) (1:1), followed by recrystallization from aqueous acetone, gave compound **9** as a white powder (yield = 82 per cent), m.p. 108–110°C.

IR (KCl) cm^{-1}: 3600–3100, 2920, 2840, 1720, 1605, 1500, 1280, 1255, 1215, 1170, 840. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·15–1·50 (m, 21H), 1·55–1·65 (m, 2H), 1·70–1·90 (m, 2H), 3·60 (t, 1H), 4·0 (t, 2H), 4·40 (sextet, 1H), 7·0 (d, 3H), 7·20–7·30 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -2·6°$ (0·0296 g ml^{-1} in $CHCl_3$).

5.2.8. *11-[1-(Oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)carboxyphenyl]undecan-1-ol (**9b**)*

This compound was prepared by a procedure analogous to that used for compound **9a**. Yield = 80 per cent, m.p. 86–88°C.

IR (KCl) cm^{-1}: 3600–3100, 2920, 2840, 1720, 1605, 1500, 1280, 1255, 1215, 1170, 840. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·15–1·55 (m, 29H), 1·55–1·65 (m, 2H), 1·70–1·90 (m, 2H), 3·60 (t, 1H), 4·0 (t, 2H), 4·40 (sextet, 1H), 7·0 (d, 3H), 7·20–7·30 (m, 4H), 7·55 (d, 2H), 8·15, (d, 2H). $[\alpha]_D = -1·8°$ (0·0191 gml^{-1} in $CHCl_3$).

5.2.9. *7-[1-(Oxy-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)carboxyphenyl]heptan-1-al (**10a**)*

The precursor alcohol (**9a**) (5 mmol) in dry dichloromethane (100 cm^3) was added to a stirred suspension of pyridinium dichromate (15 mmol), sodium acetate (45 mg) and 4 Å molecular sieves (1·5 g) in dry dichloromethane (100 cm^3) held at 0°C. The mixture was allowed to rise to room temperature and stirring was continued for 24 h. The solution was then filtered and the solvent removed *in vacuo* to leave a dark oil. Purification of the oil using flash chromatography on silica gel eluting with dichloromethane, followed by recrystallization from acetonitrile gave compound **10a** as a white powder (yield = 83 per cent). Transitions (°C), Cr 60·0 S_A 96·0 N* 105 I.

IR (KCl) cm^{-1}: 2920, 2860, 1720, 1605, 1510, 1500, 1275, 1210, 1170, 1070. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·25–1·40 (m, 15H), 1·45–1·60 (m, 2H), 1·60–1·70 (m, 2H), 1·75–1·85 (m, 2H), 2·50 (t, 2H), 4·00 (t, 2H), 4·40 (sextet, 1H), 6·95–7·10 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·20 (d, 2H), 9·80 (s, 1H). $[\alpha]_D = -1·7°$ (0·0198 gml^{-1} in $CHCl_3$).

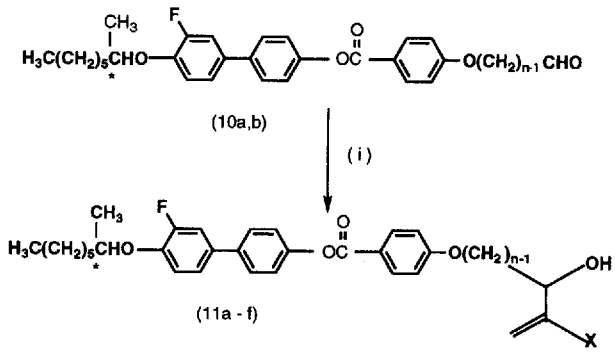
5.2.10. *11-[1-(Oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)carboxyphenyl]undecan-1-al (**10b**)*

This compound was prepared by a procedure analogous to that used for compound **10a**. Yield = 78 per cent. Transitions (°C), Cr 73·0 S_A 93·0 I.

IR (KCl) cm^{-1}: 2920, 2840, 1720, 1610, 1500, 1270, 1170, 1080, 810. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·15–1·40 (m, 23H), 1·45–1·55 (m, 2H), 1·55–1·65 (m, 2H), 1·75–1·80 (m, 2H), 2·50 (t, 2H), 4·00 (t, 2H), 4·40 (sextet, 1H), 6·95–7·05 (m, 3H), 7·20–7·35 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H), 9·75 (s, 1H). $[\alpha]_D = -2·1°$ (0·0213 gml^{-1} in $CHCl_3$).

5.3. *Scheme 3*

The process described in scheme 3 was used to synthesize the following compounds.



11a, $n=7$, $X=CN$; **11b**, $n=7$, $X=COCH_3$; **11c**, $n=7$, $X=CO_2CH_3$; **11d**, $n=11$, $X=CN$; **11e**, $n=11$, $X=COCH_3$; **11f**, $n=11$, $X=CO_2CH_3$.

(i) acrylonitrile, methyl vinyl ketone or methyl acrylate/3-quinuclidinol

Scheme 3. Synthetic route to the preparation of monomers **11a–f**.

5.3.1. *2-Cyano-3-hydroxy-8-[1-(oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenyl)carboxyphenyl]non-1-ene (**11a**)*

To a stirred solution of aldehyde **10a** (3·65 mmol) in acrylonitrile (14·6 mmol) was added 3-quinuclidinol (1·25 mmol). The reaction mixture was stirred at room temperature for 48 h. Excess of acrylonitrile was removed *in vacuo* and the residue dissolved in dichloromethane (50 cm^3). The resultant solution was washed with dilute hydrochloric acid (5 per cent v/v, 50 cm^3) followed by water (50 cm^3) and finally dried ($MgSO_4$). Removal of solvent *in vacuo* left a brown coloured solid which was purified by flash chromatography using silica gel and eluting first with dichloromethane and finally with diethyl ether. The product was recrystallized from ethanol to give compound **11a** as a white waxy solid (yield = 70 per cent). Transitions (°C), Cr 38·5 N* 66·5 I.

IR (KCl) cm^{-1}: 3600–3100, 2915, 2850, 2220, 1725, 1600, 1505, 1495, 1270, 1215, 1170, 1075. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·20–1·90 (m, 24H), 4·05 (t, 2H), 4·20 (q, 1H), 4·35 (sextet, 1H), 5·95 (s, 1H), 6·05 (s, 1H), 6·95–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -2·9°$ (0·0318 gml^{-1} in $CHCl_3$).

5.3.2. *2-Cyano-3-hydroxy-13-[1-(oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)carboxyphenyl]tridec-1-ene (**11d**)*

This compound was prepared by a procedure analogous to that used for compound **11a**, but using aldehyde **10b**. Yield = 79 per cent. Transitions (°C), Cr 35 S_C^* 67·5 S_A 75·0 I.

IR (KCl) cm^{-1}: 3700–3100, 2920, 2850, 2220, 1725, 1600, 1495, 1280, 1255, 1210, 1170, 1130, 1080, 1015. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·20–1·90 (m, 32H), 4·05 (t, 2H), 4·20 (q, 1H), 4·35 (sextet, 1H), 5·95 (s, 1H), 6·05

(s, 1H), 6·95–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -4·1°$ (0·0383 gml^{-1} in $CHCl_3$).

5.3.3. *2-Acetyl-3-hydroxy-8-[1-(oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)carboxyphenyl]non-1-ene (**11b**)*

To a stirred solution of aldehyde **10a** (3·65 mmol) in methyl vinyl ketone (3·65 mmol) and tetrahydrofuran (1·5 cm^3) was added 3-quinuclidinol (1·3 mmol). The reaction mixture was stirred for 36 h at room temperature. Excess of methyl vinyl ketone was then removed *in vacuo* and the residue was dissolved in dichloromethane (50 cm^3). The resultant solution was washed with dilute hydrochloric acid (5 per cent v/v, 50 cm^3), followed by water (50 cm^3) and then finally dried ($MgSO_4$). Removal of solvent *in vacuo* left a brown solid which was purified by flash chromatography on silica gel, eluting with dichloromethane and then with diethyl ether. Removal of solvent left compound **11b** as a white waxy solid (yield = 76 per cent). Transitions (°C), Cr 25·0 N* 44·0 I.

IR (KCl) cm^{-1}: 3600–3100, 2925, 2860, 1725, 1670, 1600, 1505, 1490, 1255, 1205, 1165, 1060, 1100, 845. ^{1}H NMR ($CDCl_3$) δ: 0·9 (t, 3H), 1·20–1·50 (m, 22H), 2·35 (d, 3H), 2·55–2·65 (m, 2H), 4·05 (t, 2H), 4·40 (quintet, 2H), 6·00 (s, 1H), 6·10 (s, 1H), 6·95–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -2·6°$ (0·0543 gml^{-1} in $CHCl_3$).

5.3.4. *2-Acetyl-3-hydroxy-13-[1-(oxy)-4-(4′-(S)-(-)-2octyloxy-3′-fluorobiphenylyl)-carboxyphenyl]tridec-1-ene (**11c**)*

This compound was prepared by a procedure analogous to that used for **11b**, but using aldehyde **10b**. Yield = 66 per cent. Transitions (°C), Cr 38·0 S_A 51·0 I.

IR (KCl) cm^{-1}: 3600–3100, 2920, 2860, 1725, 1670, 1600, 1575, 1505, 1495, 1270, 1215, 1170, 1075, 865, 845, 800, 760. ^{1}H NMR ($CDCl_3$) δ: 0·9 (t, 3H), 1·20–1·90 (m, 31H), 2·35 (s, 3H), 2·60 (d, 1H), 4·05 (t, 2H), 4·40 (quintet, 2H), 6·00 (s, 1H), 6·10 (s, 1H), 6·95–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -2·2°$ (0·0490 gml^{-1} in $CHCl_3$).

5.3.5. *2-Methylcarboxy-3-hydroxy-8-[1-(oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl)-carboxyphenyl]non-1-ene (**11c**)*

Aldehyde **10a** (3·65 mmol) was placed in methyl acrylate (14·13 mmol) and the mixture was stirred at room temperature. 3-Quinuclidinol (1·3 mmol) was added and stirring was continued for 14 days. Removal of the excess of methyl acrylate left a brown oil which was dissolved in dichloromethane (50 cm^3). The resultant solution was washed with dilute hydrochloric acid (5 per cent v/v, 50 cm^3), followed by water (50 cm^3) and then dried ($MgSO_4$). Removal of solvent *in vacuo* left a brown waxy solid which was purified using flash chromatography on silica gel, eluting with dichloromethane and then with diethyl ether to leave, after removal of the solvent, a white waxy solid (yield = 65 per cent). Transitions (°C), Cr 25·0 N*40·0 I.

IR (KCl) cm^{-1}: 3600–3100, 2920, 2860, 1720, 1600, 1505, 1495, 1255, 1200, 1165, 1060, 1050, 840, 760. ^{1}H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·20–1·50 (m, 16H), 1·55–1·70 (m, 2H), 1·70–1·90 (m, 4H), 2·55 (d, 1H), 3·75 (s, 3H), 4·05 (t, 3H), 4·40 (sextet, 2H), 5·80 (s, 1H), 6·20 (s, 1H), 6·90–7·10 (m, 3H), 7·15–7·30 (m, 4H), 7·45–7·60 (m, 2H), 8·10–8·20 (m, 2H). $[\alpha]_D = -2·4°$ (0·0324 gml^{-1} in $CHCl_3$).

5.3.6. *2-Methylcarboxy-3-hydroxy-8-[1-(oxy)-4-(4′-(S)-(-)-2-octyloxy-3′-fluorobiphenylyl) carboxyphenyl]tridec-1-ene (**11f**)*

This compound was prepared by a procedure analogous to that used for **11c**, but using aldehyde **10b**. Yield = 55 per cent. Transitions (°C), Cr 48·0 S_A 61·0 I.

IR (KCl) cm^{-1}: 3650–3100, 1720, 1600, 1505, 1495, 1270, 1215, 1170, 1075, 840. ^{1}H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·20–1·50 (m, 25H), 1·55–1·70 (m, 2H), 1·70–1·90 (m, 4H), 3·75 (s, 3H), 4·05 (t, 3H), 4·40 (sextet, 2H), 5·80 (s, 1H), 6·20 (s, 1H), 6·95–7·10 (m, 3H), 7·20–7·30 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H). $[\alpha]_D = -2·6°$ (0·0279 gml^{-1} in $CHCl_3$).

5.4. *Scheme 4*

A number of oligomers were prepared by the scheme 4 procedure described in detail below for the oligomerisation of monomer **11a**. Yield and characterization data are given for each oligomerisation.

5.4.1. *Oligomerization of monomer (**11a**)*

Monomer **11a** (1·10 mmol) and Irgacure 184 (Ciba–Geigy) (0·06 mmol) were dissolved in dichloromethane (3·0 cm^3) and the solution was spread on a 25 × 18 cm borosilicate glass plate. The solvent was allowed to evaporate to leave a thin monomer film. A similar 25 × 18 cm glass plate was placed over the monomer film and the two plates were squeezed together to reduce the thickness of the monomer film further. The monomer 'sandwich' was then irradiated for 3 h under a Philips UVA sunlamp (75 W). The resultant oligomer was dissolved in dichloromethane and the solution added dropwise to methanol in four 30 cm^3 centrifuge tubes to form a heavy, white suspension. The tubes were centrifuged for 30 min at 5000 rpm and afterwards, the oligomer was redissolved in dichloromethane (10 cm^3). Precipitation in methanol and centrifugation were carried out a further two times (to remove all the unreacted monomer) and then the oligomer was finally dissolved

again in dichloromethane (10 cm^3). The solution was then passed through a membrane filter (0·5 μm) and the solvent removed to leave, after thorough drying *in vacuo*, the oligomer as a glassy solid (yield 50 per cent).

IR (KCl) cm^{-1}: 3600–3200, 2925, 2860, 2220, 1725, 1600, 1505, 1495, 1260, 1205, 1165, 1070, 760. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·15–1·70 (m, 23H), 1·75–1·95 (s, 4H), 3·85–4·05 (s, 2H), 4·30–4·45 (m, 1H), 6·80–7·05 (s, 3H), 7·10–7·40 (m, 4H), 7·45–7·60 (s, 2H), 7·95–8·15 (s, 2H).

5.4.2. *Oligomerization of monomer (**11b**)*

Yield = 44 per cent. IR (KCl) cm^{-1}: 3600–3200, 2925, 2855, 1720, 1600, 1505, 1490, 1255, 1200, 1160, 1060, 1010, 845, 760. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·15–1·70 (m, 22H), 1·75–1·95 (s, 4H), 2·00–2·50 (m, 4H), 3·85–4·05 (s, 2H), 4·30–4·45 (m, 1H), 6·80–7·05 (s, 3H), 7·10–7·40 (m, 4H), 7·45–7·60 (s, 2H), 8·05–8·15 (m, 2H).

5.4.3. *Oligomerization of monomer (**11c**)*

Yield = 49 per cent. IR (KCl) cm^{-1}: 3650–3150, 2930, 2860, 1730, 1710, 1600, 1575, 1505, 1490, 1360, 1255, 1200, 1165, 760. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·05–1·75 (m, 22H), 1·75–1·95 (m, 4H), 3·50–3·80 (s, 3H), 4·00 (m, 2H), 4·35 (sextet, 1H), 6·90–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (m, 2H), 8·15 (m, 2H).

5.4.4. *Oligomerization of monomer (**11d**)*

Yield = 48 per cent. IR (KCl) cm^{-1}: 3600–3200, 2920, 2850, 1725, 1600, 1500, 1490, 1255, 1205, 1165, 1170, 1070, 760. ^1H NMR ($CDCl_3$) δ: 0·85–0·95 (m, 3H), 1·15–1·90 (m, 35H), 4·0 (s, 2H), 4·40 (q, 1H), 6·90–7·05 (m, 3H), 7·15–7·30 (m, 4H), 7·50–7·60 (m, 2H), 8·10–8·20 (m, 2H).

5.4.5. *Oligomerization of monomer (**11e**)*

Yield = 35 per cent. IR (KCl) cm^{-1}: 2920, 2860, 1725, 1600, 1505, 1495, 1260, 1210, 1165, 1070, 760. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·10–1·65 (m, 30H), 1·70–1·90 (m, 4H), 2·05–2·40 (m, 4H), 3·95–4·05 (m, 2H), 4·40 (sextet, 1H), 6·95–7·05 (m, 3H), 7·20–7·30 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H).

5.4.6. *Oligomerization of monomer (**11f**)*

Yield = 48 per cent. IR (KCl) cm^{-1}: 3600–3200, 1730, 1600, 1505, 1495, 1260, 1210, 1165. ^1H NMR ($CDCl_3$) δ: 0·85 (t, 3H), 1·10–1·70 (m, 30H), 1·75–1·95 (m, 5H), 3·50–3·80 (s, 3H), 4·00 (m, 2H), 4·35 (sextet, 1H), 6·90–7·05 (m, 3H), 7·25–7·40 (m, 4H), 7·55 (d, 2H), 8·15 (d, 2H).

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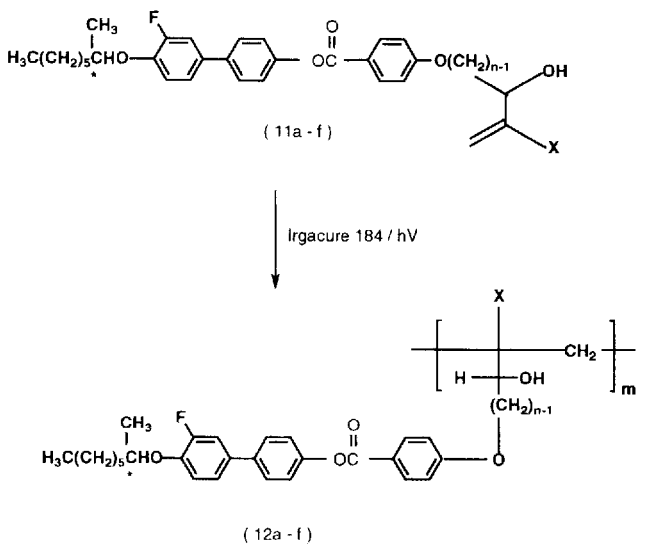

12a, $n=7$, $X=CN$; **12b**, $n=7$, $X=COCH_3$; **12c**, $n=7$, $X=CO_2CH_3$; **12d**, $n=11$, $X=CN$; **12e**, $n=11$, $X=COCH_3$; **12f**, $n=11$, $X=CO_2CH_3$.

Scheme 4. Synthetic route to the preparation of oligomers **12a–f**.

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