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Side-chain liquid crystal polymers derived from oxetane monomers containing 2- or 3-fluorophenyl moieties in the core of the mesogen†

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Two series of side-chain liquid crystalline polymers were prepared by cationic ring-opening of oxetane substituted mesogens. Each of the terminally appended side chain polymers prepared had a flexible spacer length of six methylene units separating a mesogenic aromatic core from the polymer backbone. The core unit was designed to incorporate either a 2-fluoro- or a 3-fluoro-phenyl unit possessing either an (*R*)-(−)-1-methylheptyl, (*S*)-(+)-2-methylbutyl or a 1-propylbutyl terminal chain. The materials produced in this study were compared with the previously reported unsubstituted parent materials in order to assess the affect of having a lateral fluoro substituent in the core. Low melting points, smectic C/C* and smectic A/A* phases were exhibited by most of the monomers. The behaviour of the 3-fluorophenyl monomers was found to be similar to their unfluorinated parents, whereas the 2-fluoro analogues were shown to have significantly lower transition temperatures. All of the polymers exhibited smectic C/C* and smectic A/A* phases over wide temperature ranges and had relatively low T_g values. Some of the polymers were found to exhibit exceptionally large temperature ranges for the smectic C/C* phase, *e.g.* from 0.8 °C to 190 °C.

Introduction

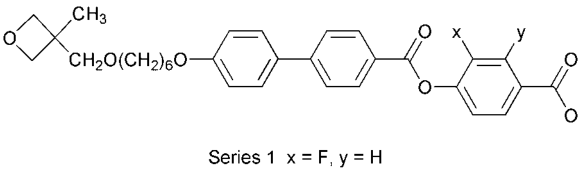
Ferroelectric side-chain liquid crystal polymers (SCLCP) have been an active area of research in liquid crystals since the first example reported by Shibaev *et al.*[1] in 1984. Most of the early work on SCLCP's was based on poly(acrylate)s, although in 1987 Hahn and Percec[2] reported the first poly(siloxane) based material to exhibit a ferroelectric SmC* phase. Both these polymer backbones have provided the basis for the majority of work on SCLCP's even though poly(oxyethylene) materials[3] and polymers with more unusual backbones[4,5] have also been reported.

In order to study ferroelectric responses to applied electric fields, SCLCP's need to be designed in such a way that the terminally appended mesogenic core units are separated from the polymer backbone by a flexible spacer group so that the motions of the mesogenic units are decoupled from those of the backbone.[6] Hsu *et al.*[7] showed that polymers which exhibit smectic C phases are typically exhibited by SCLCP's where the length of the flexible spacer is greater than six methylene units. It was also shown that an increase in the flexibility of the backbone increases the tendency for smectic C phases to be exhibited.[7] Even when a polymer has been designed to exhibit a chiral smectic C* phase, the flexibility of the polymer backbone is an important factor in determining the speed of the response of the polymer to an applied electric field. It has been reported that polymers with relatively flexible backbones will respond more quickly to applied fields than polymers with more rigid backbones,[8] and for this reason poly(siloxane)s are found to respond faster than poly(oxyethylene)s which in turn respond faster than poly(acrylate)s.

In previous studies[9] we described the synthesis of a series of SCLCP obtained *via* the cationic ring-opening polymerisation of oxetane monomers; the resulting polymers were shown to exhibit smectic C phases with wide temperature ranges and low glass transition temperatures in addition to possessing reasonably high DP values (~20). The defect textures, observed *via* transmitted polarized light microscopy, exhibited large domains typical of low molar mass materials. The defect textures formed after very short annealing times thereby indicating that the polymers had relatively low viscosities. In this article we report the synthesis and mesomorphism of two new series of low molar mass oxetanes and their corresponding polymers that possess either a 2-fluorophenyl or a 3-fluorophenyl moiety (series 1 and 2 in Fig. 1) in their mesogenic cores. The general structures of these systems are shown in Fig. 1, with the materials being direct analogues of the unsubstituted parent system previously described.[9]

Experimental

Compounds **1**, **10**, **24** and 1,6-dibromohexane were purchased from Aldrich and compound **21** was purchased from E. Merck; all of these materials were used without further purification. The structures of the products and intermediates were analysed using a range of spectral techniques including ^{1}H NMR spectrometry (JEOL JNM-LA400 FT 400 MHz spectrometer, where the spectra, unless otherwise stated, were recorded in $CDCl_3$ using Me_4Si as an internal standard; the *J* values are given in Hz), infra-red spectrometry (Perkin-Elmer 983G infra-red spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC-MS spectrometer). The purifications of the intermediates and final products was achieved using column chromatography over C60, 230–400 mesh silica gel (Merck). The optical rotations



Series 1 x = F, y = H

Series 2 x = H, y = F

Fig. 1 The structure of the monomers in this work.

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†Electronic supplementary information (ESI) available: a colour version of Fig. 4. See http://www.rsc.org/suppdata/jm/b0/b009426i/

of the chiral intermediates and products was measured using an Optical Activity AA-10 automatic polarimeter and the $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Examination of the mesomorphic behaviour and the determination of transition temperatures of the materials was achieved using transmitted polarized-light microscopy (Mettler FP5 temperature controller unit in conjunction with a Mettler FP52 hot-stage linked to an Olympus BH2 microscope). The transition temperatures were verified and the enthalpies of transition were determined by thermal analysis using a Perkin-Elmer DSC7 differential scanning calorimeter using DSC7/UNIX software.

The molecular weights of the polymers and polydispersities were determined *via* GPC analyses using two mixed D, PL gel columns, 30 cm × 0.75 cm, 5 µm, calibrated with polystyrene standards of a molecular weight of 1000–430 500 amu.

All of the monomeric systems were found to give satisfactory elemental analyses.

Molecular modelling studies were performed using a Silicon Graphics workstation (Indigo XS24, 4000) with the programs Quanta and CHARMm. Within CHARMm, the Adopted Basis Newton Raphson (ABNR) algorithm was used to locate the molecular conformation with the lowest potential energy. The minimisation calculations were performed until the root mean square (RMS) force reached 4.184 kJ mol^{-1} Å^{-1}, which is close to the resolution limit. The RMS force is a direct measure of the tolerance applied to the energy gradient (*i.e.*, the rate of change of potential energy with step number) during each cycle of minimisation. The calculation was terminated in cases where the average energy gradient was less than the specified value. The results of the molecular mechanics calculations were generated using the programs QUANTA V 4.0 and CHARMm V22.2. The programs were developed and integrated by Molecular Simulations Inc., Cambridge, UK. The modelling packages assume the molecules to be a collection of hard particles held together by elastic forces, in the gas phase at absolute zero in an ideal motionless state, and the force fields used are those described in CHARMm V 22.2.

The synthetic scheme for the preparation of intermediates **7**–**9** (Scheme 1) has been well documented in the literature by Parghi *et al.*[10,11] and for brevity will not be reported in detail, however the physical properties and the spectral data are reported.

(*R*)-(−)-1-Methylheptyl 3-fluoro-4-hydroxybenzoate (7)

$[\alpha]_D^{25} = -33.7$ (*c* 0.03829 in $CHCl_3$). δ_H: 0.88 (3H, t, *J* 6), 1.22–1.40 (8H, m), 1.30 (3H, d, *J* 6), 1.52–1.78 (2H, m), 5.12 (1H, sextet, *J* 6), 6.28 (1H, br s), 7.02 (1H, t, *J* 9), 7.72–7.76 (1H, m), 7.78 (1H, s). ν_{max} (film)/cm^{-1}: 3340, 3020, 2920, 2860, 1700, 1610, 1590, 1510, 1440, 1300, 1210, 900, 760. *m*/*z*: 268 (M^+), 156, 139, 112, 58, 43 (100%).

(*S*)-(+)-2-Methylbutyl 3-fluoro-4-hydroxybenzoate (8)

$[\alpha]_D^{25} = +5.18$ (*c* 0.04615 in $CHCl_3$). δ_H: 0.94 (3H, t, *J* 6), 1.00 (3H, d, *J* 6), 1.28 (1H, octet, *J* 6), 1.53 (1H, octet, *J* 6), 1.83 (1H, octet, *J* 6), 4.14 (2H, m), 6.06 (1H, br s), 7.03 (1H, t, *J* 9), 7.72–7.78 (1H, m), 7.79 (1H, t, *J* 2). ν_{max} (film)/cm^{-1}: 3350, 2970, 2880, 1690, 1620, 1600, 1520, 1440, 1310, 1220, 1120, 1090, 980, 900, 840, 770. *m*/*z*: 226 (M^+), 156, 139, 82, 70, 43 (100%).

1-Propylbutyl 3-fluoro-4-hydroxybenzoate (9)

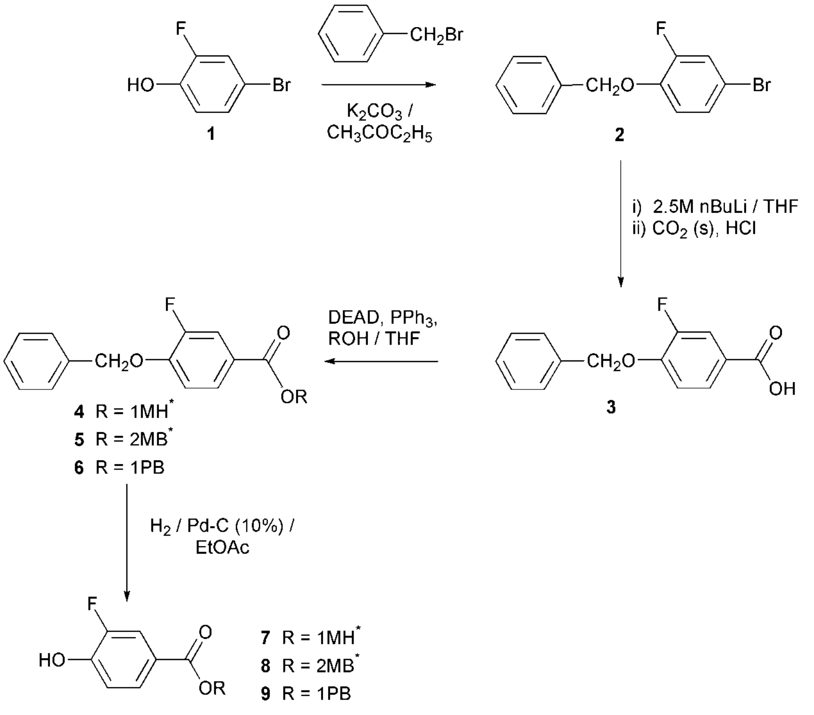
δ_H: 0.92 (6H, t, *J* 6), 1.30–1.48 (4H, m), 1.58–1.76 (4H, m), 5.14 (1H, quintet, *J* 6), 7.03 (1H, t, *J* 9), 7.72–7.77 (1H, m), 7.80 (1H, t, *J* 2), phenolic proton not observed. ν_{max} (KBr disc)/cm^{-1}: 3340, 2960, 2880, 1690, 1620, 1600, 1520, 1440, 1300, 1220, 1120, 1090, 950, 900, 840, 770. *m*/*z*: 254 (M^+), 139, 111, 98, 83, 43 (100%).

The preparation of intermediate **11** (Scheme 2) has been reported previously.[12]

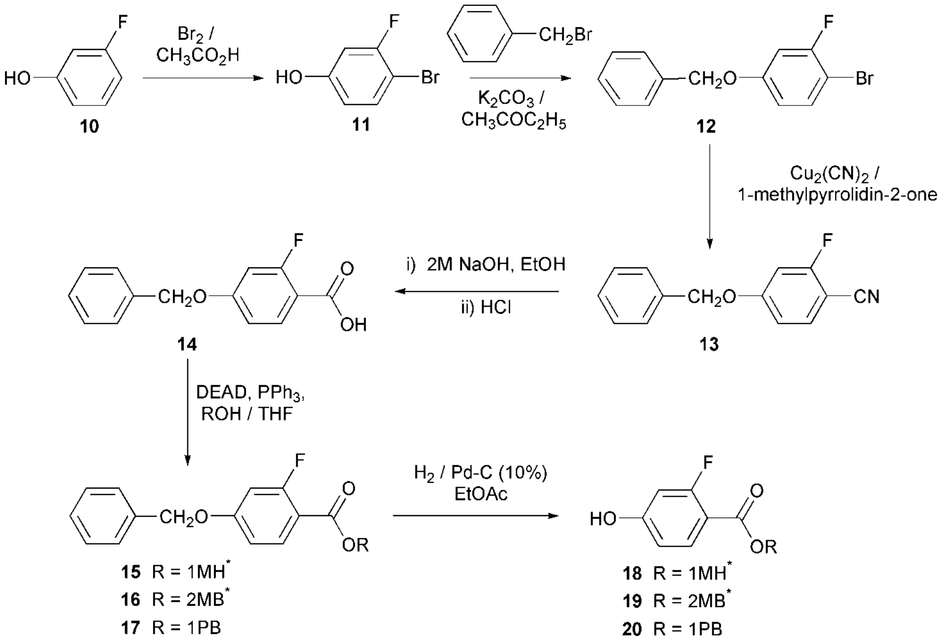
4-Benzyloxy-1-bromo-2-fluorobenzene (12)

The experimental procedure was the same as for the preparation of compound **2**. The following quantities were used: compound **11**, 36.80 g, 0.19 mol; potassium carbonate, 31.74 g, 0.23 mol; benzyl bromide, 35.70 g, 0.21 mol; butanone, 500 ml. Yield 56.20 g (96%), mp 33.2–34.6 °C.

δ_H: 5.05 (2H, s), 6.69 (1H, ddd, J_1 10, J_2 8, J_3 4), 6.77 (1H, dd, J_2 8, J_3 4), 7.32–7.42 (6H, m). ν_{max} (KBr disc)/cm^{-1}: 1600, 1580, 1480, 1410, 1315, 1260, 1240, 1170, 1000, 960, 830, 760, 730, 690, 650. *m*/*z*: 282, 280 (M^+), 191, 189, 91 (100%), 65.



Scheme 1 Synthetic route to 3-fluoro-4-hydroxybenzoates (1MH = 1-methylheptyl; 2MB = 2-methylbutyl; 1PB = 1-propylbutyl).



Scheme 2 Synthetic route to 2-fluoro-4-hydroxybenzoates.

4-Benzyloxy-2-fluorobenzonitrile (13)

Compound **12** (10.00 g, 35.7 mmol) and copper(I) cyanide (13.00 g, 71.4 mmol) were suspended in 1-methylpyrrolidin-2-one (250 ml) and heated under reflux for 24 h. The reaction mixture was cooled to room temperature and filtered through 'Hyflo supercel®'. Water (200 ml) was added to the filtrate which was then washed with ether (2 × 400 ml). The combined ether extracts were washed with water (2 × 500 ml) and brine (500 ml) and then dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* to yield an off-white solid which was purified by column chromatography (dichloromethane) to yield colourless crystals which were recrystallised (cyclohexane) and dried *in vacuo*. Yield 5.79 g (71%), mp 77.7–79.5 °C.

δ_H: 5.10 (2H, s), 6.74–6.87 (2H, m), 7.34–7.42 (5H, m), 7.52 (1H, t, *J* 9). ν_{max} (KBr disc)/cm^{-1}: 2240, 1610, 1570, 1500, 1450, 1380, 1290, 1260, 1110, 1000, 910, 850, 810, 770, 740, 700, 630, 510. *m*/*z*: 227 (M^+), 156, 91 (100%), 65.

4-Benzyloxy-2-fluorobenzoic acid (14)

Compound **13** (5.70 g, 25 mmol) was suspended in a 2.5 M sodium hydroxide solution [10.00 g in water (100 ml)] and heated under reflux for 60 h. The solution was then acidified with conc. hydrochloric acid to pH 3 and the mixture was then washed with ether (2 × 100 ml). The carboxylic acid was then extracted from the combined ether solutions with a saturated sodium bicarbonate solution (200 ml) and the alkaline extract was acidified with conc. hydrochloric acid. The mixture was then washed with ether (400 ml) and the organic washings were washed with brine (2 × 200 ml) and dried (Na_2SO_4). The drying agent was filtered off and the solvent removed *in vacuo* to yield a colourless solid which was recrystallised [cyclohexane–ethyl acetate (95 : 5)]. Yield 3.85 g (58%), mp 165.3–167.6 °C.

δ_H: 5.10 (2H, s), 6.68–6.83 (2H, m), 7.30–7.45 (5H, m), 7.91 (1H, t, *J* 9), acidic proton was not detected. ν_{max} (KBr disc)/cm^{-1}: 2920, 1700, 1610, 1500, 1440, 1410, 1340, 1270, 1240, 1050, 1020, 900, 840, 740, 650. *m*/*z*: 246 (M^+), 229, 139, 127, 91 (100%), 65.

(*R*)-(−)-1-Methylheptyl 4-benzyloxy-2-fluorobenzoate (15)

The experimental procedure was the same as for the preparation of compound **4**. The following quantities were used: compound **14**, 8.00 g, 33 mmol; (*S*)-(+)-octan-2-ol, 4.29 g, 33 mmol; triphenylphosphine, 9.24 g, 35 mmol; DEAD, 5.74 g, 33 mmol in THF, 40 ml; THF, 150 ml. Yield 8.20 g (69%), $[\alpha]_D^{24} = -25.32$ (*c* 0.07371 in $CHCl_3$).

δ_H: 0.82 (3H, t, *J* 6), 1.20–1.44 (8H, m), 1.31 (3H, t, *J* 6), 1.50–1.62 (1H, m), 1.66–1.77 (1H, m), 5.04 (2H, s), 5.11 (1H, sextet, *J* 6), 6.68 (1H, dd, J_1 8, J_2 2), 6.77 (1H, dd, J_1 8, J_2 2), 7.30–7.43 (5H, m), 7.86 (1H, t, *J* 9). ν_{max} (film)/cm^{-1}: 2960, 2930, 2860, 1710, 1620, 1580, 1500, 1450, 1440, 1380, 1280, 1265, 1170, 1140, 1120, 1090, 1025, 890, 820, 740, 700. *m*/*z*: 358 (M^+), 338, 229, 138, 110, 91 (100%).

(*S*)-(+)-2-Methylbutyl 4-benzyloxy-2-fluorobenzoate (16)

The experimental procedure was the same as for the preparation of compound **4**. The following quantities were used: compound **14**, 8.00 g, 33 mmol; (*S*)-(−)-2-methylbutan-1-ol, 2.90 g, 33 mmol; DEAD, 5.74 g, 33 mmol; triphenylphosphine in THF, 9.24 g, 35 mmol in 40 ml; THF, 150 ml. Yield 9.67 g (93%), $[\alpha]_D^{24} = +3.58$ (*c* 0.0401 $CHCl_3$).

δ_H: 0.94 (3H, t, *J* 6), 1.00 (3H, d, *J* 6), 1.26 (1H, octet, *J* 6), 1.52 (1H, octet, *J* 6), 1.83 (1H, octet, *J* 6), 4.14 (2H, m), 5.10 (2H, s), 6.70 (1H, dd, J_1 8, J_2 2), 6.78 (1H, dd, J_1 8, J_2 2), 7.30–7.42 (5H, m), 7.90 (1H, t, *J* 9). ν_{max} (film)/cm^{-1}: 2960, 2940, 2880, 1710, 1620, 1580, 1500, 1280, 1265, 1175, 1140, 1000, 910, 840, 740, 700. *m*/*z*: 316 (M^+), 246, 199, 183, 110, 91 (100%), 65.

1-Propylbutyl 4-benzyloxy-2-fluorobenzoate (17)

The experimental procedure was the same as for the preparation of compound **4**. The following quantities were used: compound **14**, 9.95 g, 40 mmol; heptan-4-ol, 4.64 g, 40 mmol; DEAD, 6.96 g, 40 mmol; triphenylphosphine in THF, 11.53 g, 44 mmol in 40 ml; THF, 150 ml. Yield 4.92 g (40%).

δ_H: 0.93 (6H, t, *J* 6), 1.32–1.48 (4H, m), 1.54–1.73 (4H, m), 5.08 (2H, s), 5.15 (1H, quintet, *J* 6), 6.70 (1H, dd, J_1 8, J_2 2), 6.78 (1H, dd, J_1 8, J_2 2), 7.32–7.43 (5H, m), 7.89 (1H, t, *J* 9). ν_{max} (film)/cm^{-1}: 2960, 2940, 2880, 1710, 1620, 1580, 1505, 1440, 1280, 1270, 1170, 1150, 1130, 1090, 1030, 900, 840, 740, 700. *m*/*z*: 344 (M^+), 247, 229, 91 (100%), 65.

(*R*)-(−)-1-Methylheptyl 4-hydroxy-2-fluorobenzoate (18)

The experimental procedure was the same as for the preparation of compound **7**. The following quantities were used: compound **15**, 8.20 g, 23 mmol; 10% palladium-on-charcoal, 0.30 g; ethyl acetate, 200 ml. Yield 4.68 g (76%), $[\alpha]_D^{25} = -28.39$ (*c* 0.03202 in $CHCl_3$).

δ_H: 0.86 (3H, t, *J* 6), 1.20–1.46 (8H, m), 1.30 (3H, d, *J* 6), 1.54–1.77 (2H, m), 5.12 (1H, sextet, *J* 6), 6.64 (1H, dd, J_1 8, J_2 2), 6.70 (1H, dd, J_1 8, J_2 2), 7.84 (1H, t, *J* 9), phenolic proton was not observed. ν_{max} (film)/cm^{-1}: 3370, 2930, 2860, 1690, 1620, 1600, 1510, 1460, 1290, 1250, 1230, 1150, 1120, 1090, 980, 920, 855, 775. *m*/*z*: 268 (M^+), 157, 139 (100%), 112, 83, 55.

(*S*)-(+)-2-Methylbutyl 4-hydroxy-2-fluorobenzoate (19)

The experimental procedure was the same as for the preparation of compound **7**. The following quantities were used: compound **16**, 9.67 g, 31 mmol; 10% palladium-on-charcoal, 0.30 g; ethyl acetate, 300 ml. Yield 5.46 g (78%), $[\alpha]_D^{25} = +6.11$ (*c* 0.1174 in $CHCl_3$).

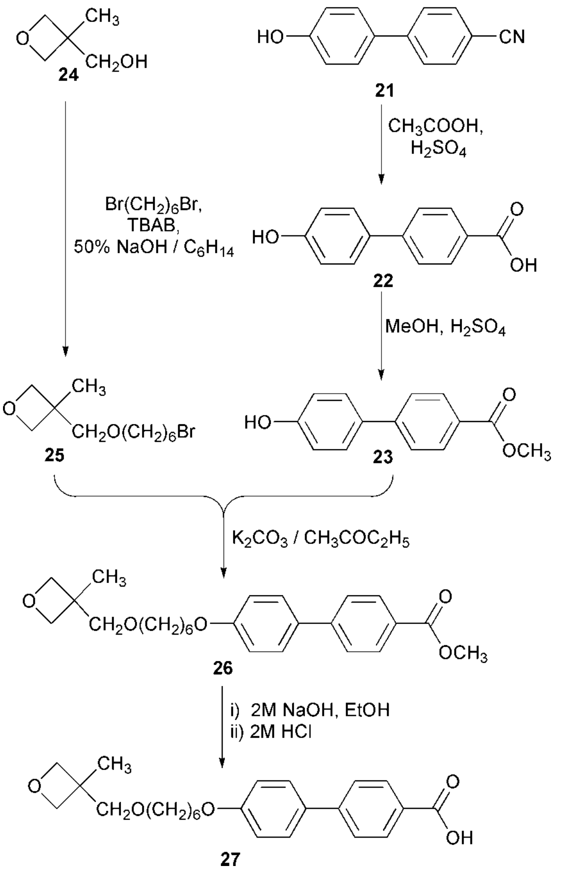
δ_H: 0.95 (3H, t, *J* 6), 1.02 (2H, d, *J* 6), 1.28 (1H, octet, *J* 6), 1.58 (1H, octet, *J* 6), 1.84 (1H, octet, *J* 6), 4.15 (2H, m), 5.90 (1H, br s), 6.62 (1H, dd, J_1 8, J_2 2), 6.67 (1H, dd, J_1 8, J_2 2), 7.86 (1H, t, *J* 9), phenolic proton not observed. ν_{max} (KBr disc)/cm^{-1}: 3370, 2960, 2940, 2900, 2880, 1700, 1680, 1620, 1595, 1510, 1460, 1390, 1375, 1320, 1300, 1250, 1225, 1140, 1095, 1020, 940, 850, 765, 640. *m*/*z*: 226 (M^+), 157, 139 (100%), 111, 83, 70.

1-Propylbutyl 4-hydroxy-2-fluorobenzoate (20)

The experimental procedure was the same as for the preparation of compound **7**. The following quantities were used: compound **17**, 4.92 g, 14 mmol; 10% palladium-on-charcoal, 0.20 g; ethyl acetate, 200 ml. Yield 3.49 g (98%).

δ_H: 0.90 (6H, t, *J* 6), 1.31–1.47 (4H, m), 1.54–1.72 (4H, m), 5.14 (1H, quintet, *J* 6), 6.64 (1H, dd, J_1 8, J_2 2), 6.65 (1H, dd, J_1 8, J_2 2), 7.84 (1H, t, *J* 9), phenolic proton not observed. ν_{max} (KBr disc)/cm^{-1}: 3330, 2960, 2940, 2880, 1690, 1670, 1620, 1510, 1470, 1330, 1300, 1250, 1140, 1100, 975, 850, 770, 690, 620. *m*/*z*: 254 (M^+), 157, 139 (100%), 98, 83, 56.

The preparation of intermediates **22**,[13] **23**[14] and **25**[15] (Scheme 3) have been reported previously.



Scheme 3 Synthetic route to carboxylic acid intermediates.

Methyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (26)

Compound **23** (29.6 g, 0.13 mol), compound **25** (34.7 g, 0.13 mol), potassium carbonate (35.9 g, 0.26 mol) and potassium iodide (5.00 g, 30 mmol) were dissolved in butanone (700 ml) and heated under reflux overnight. On completion of the reaction (analysis by TLC), the reaction solution was cooled to room temperature, poured into water (200 ml) and stirred for 2 h. The resulting colourless precipitate was filtered off, washed with water and dried *in vacuo* (P_2O_5). Yield 32.8 g (62%), mp 146–147.3 °C.

δ_H: 1.32 (3H, s), 1.40–1.54 (4H, m), 1.62 (2H, quintet, *J* 6), 1.82 (2H, quintet, *J* 6), 3.46 (4H, s and t, *J* 6), 3.91 (3H, s), 3.99 (2H, t, *J* 6), 4.35 (2H, d, *J* 6), 4.51 (2H, d, *J* 6), 6.99 (2H, d, *J* 8), 7.56 (2H, d, *J* 8), 7.62 (2H, d, *J* 8), 8.08 (2H, d, *J* 8). ν_{max} (KBr disc)/cm^{-1}: 3400, 2940, 2860, 1710, 1600, 1525, 1490, 1290, 1250, 1200, 1110, 830. *m*/*z*: 412 (M^+), 228 (100%), 197, 139, 115, 83, 55.

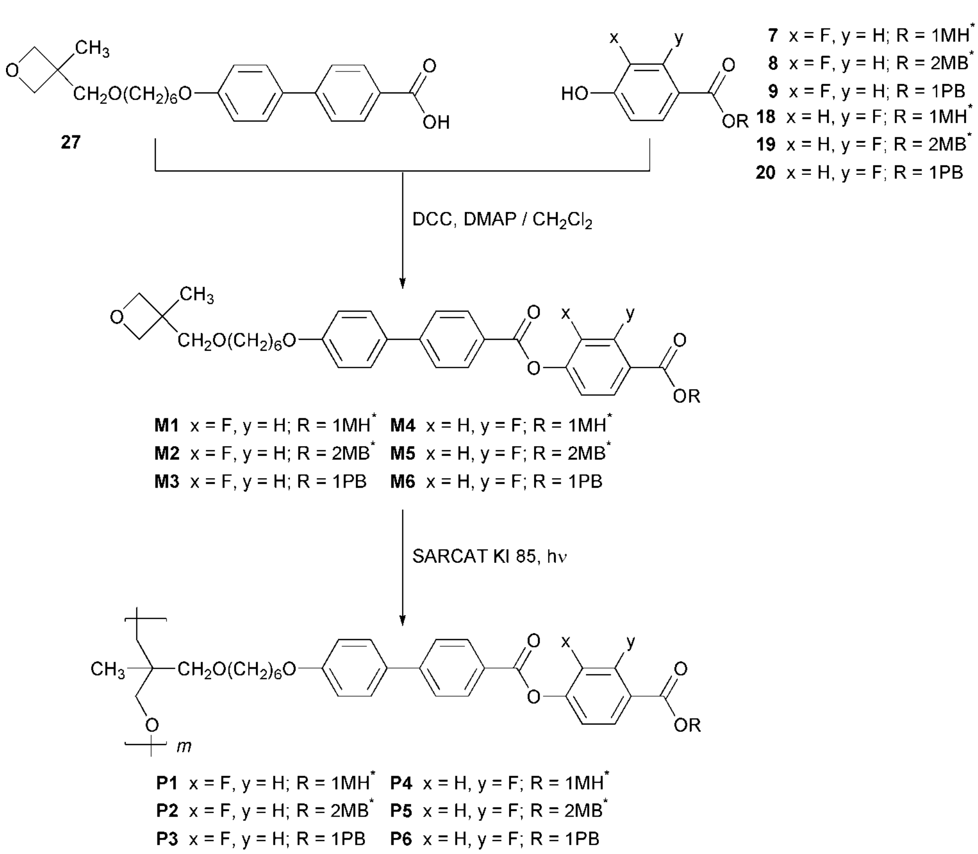
4′-[6-(3-Methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylic acid (27)

10 M Sodium hydroxide (30 ml) was added to a solution of compound **26** (32.8 g, 0.080 mol) in ethanol–water (1 : 5) (1.6 l) and the mixture was heated under reflux for 1 h. The reaction mixture was cooled in an ice–salt bath and 2 M hydrochloric acid was slowly added until the solution was acidic (pH 6) and the solution was left to stir for 1 h. The colourless solid formed was filtered off and washed with copious amounts of water until the washings were neutral and dried (P_2O_5). Yield 27.0 g (84%); K 155.4 N 178.2 Iso liq. °C.

δ_H: 1.32 (3H, s), 1.41–1.54 (4H, m), 1.64 (2H, quintet, *J* 6), 1.84 (2H, quintet, *J* 6), 3.48 (4H, s and t, *J* 6), 3.99 (2H, t, *J* 6), 4.37 (2H, d, *J* 6), 4.53 (2H, d, *J* 6), 6.98 (2H, d, J 8), 7.58 (2H, d, *J* 8), 7.64 (2H, d, *J* 8), 8.14 (2H, d, *J* 8), acid proton not observed. ν_{max} (KBr disc)/cm^{-1}: 3430, 2940, 2860, 1700, 1670, 1600, 1520, 1490, 1430, 1290, 1250, 1190, 1110, 940, 830. *m*/*z*: 398 (M^+), 228, 214 (100%), 197, 83, 55.

(*R*)-(−)-4-(1-Methylheptyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M1) (Scheme 4)

N,*N*′-Dicyclohexylcarbodiimide (DCC) (0.64 g, 3.10 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.10 g, 0.10 mmol) were added to a stirred solution of compound **27** (1.23 g, 3.10 mmol) and compound **7** (0.83 g, 3.10 mmol) in dichloromethane. The reaction mixture was left stirring at room temperature for 72 h until completion. The dicyclohexylurea formed was filtered off and the solvent removed *in vacuo* to yield a viscous colourless oil which was purified by column chromatography (ethyl acetate). The colourless material was then recrystallised from ethanol by cooling to −60 °C, filtered off and dried *in vacuo* (P_2O_5). Yield 1.83 g (91%), $[\alpha]_D^{24} = -22.3$ (*c* 0.02997 in $CHCl_3$); K < −70 SmC* 40.0 SmA* 61.6 Iso liq. °C. Elemental analysis for $C_{39}H_{49}F_1O_7$: calculated C 72.18%; H 7.62%; found C 72.02%; H 7.57%. δ_H: 0.88 (3H, t, *J* 6), 1.29 (3H, s), 1.21–1.41 (8H, m), 1.34 (3H, d, *J* 6), 1.42–1.54 (4H, m), 1.64 (4H, quintet, *J* 6), 1.83 (2H, quintet, *J* 6), 3.48 (2H, t, *J* 6), 3.50 (2H, s), 4.04 (2H, t, *J* 6), 4.37 (2H, d, *J* 6), 4.52 (2H, d, *J* 6), 5.17 (1H, sextet, *J* 6), 7.00 (2H, d, *J* 8), 7.34 (1H, dd, J_1 9, J_2 1), 7.58 (2H, d, *J* 8), 7.70 (2H, d, *J* 8), 7.85–7.94 (2H, m), 8.22 (2H,



Scheme 4 Synthetic route to the oxetane monomers and polymers. m = number of repeat units.

d, J 8). ν_{max} (film)/cm^{-1}: 2940, 2860, 1740, 1715, 1600, 1505, 1450, 1430, 1290, 1260, 1180, 1110, 1060, 1015, 900, 830, 770. m/z: 648 (M$^+$), 479, 381 (100%), 196, 139, 55.

(*S*)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M2)

The experimental procedure was the same as for the preparation of compound **M1**. The following quantities were used: compound **27**, 1.31 g, 3.30 mmol; compound **8**, 0.75 g, 3.30 mmol; DCC, 0.68 g, 3.30 mmol; DMAP, 0.10 g, 0.10 mmol; dichloromethane, 50 ml. Yield 1.50 g (75%), $[\alpha]_D^{25} = +1.0$ (c 0.01227 in CHCl$_3$); K 0.8 SmC* 51.9 SmA* 89.6 N* 95.5 BP III 99.0 Iso liq. °C. Elemental analysis for $C_{36}H_{43}F_1O_7$: calculated C 71.25%; H 7.15%; found C 71.32%; H 7.13%.

δ_H: 0.97 (3H, t, J 6), 1.02 (3H, d, J 6), 1.31 (3H, s), 1.40–1.56 (6H, m), 1.63 (2H, quintet, J 6), 1.83 (3H, quintet, J 6; and octet, J 6), 3.47 (2H, s), 3.48 (2H, t, J 6), 4.01 (2H, t, J 6), 4.19 (2H, m), 4.36 (2H, d, J 6), 4.52 (2H, d, J 6), 7.01 (2H, d, J 8), 7.36 (1H, dd, J_1 9, J_2 1), 7.61 (2H, d, J 8), 7.70 (2H, d, J 8), 7.86–7.94 (2H, m), 8.24 (2H, d, J 8). ν_{max} (film)/cm^{-1}: 2940, 2870, 1730, 1710, 1605, 1510, 1460, 1360, 1270, 1220, 1180, 1115, 1055, 1015, 980, 890, 830, 765. m/z: 606 (M$^+$), 381 (100%), 351, 197, 139, 55.

4-(1-Propylbutyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M3)

The experimental procedure was the same as for the preparation of compound **M1**. The following quantities were used: compound **27**, 1.25 g, 3.15 mmol; compound **9**, 0.76 g, 3.15 mmol; DCC, 0.65 g, 3.15 mmol; DMAP, 0.10 g, 0.10 mmol; dichloromethane, 50 ml. Yield 1.60 g (80%); SmC 10.3 Iso liq. °C. Elemental analysis for $C_{38}H_{47}F_1O_7$: calculated C 71.89%; H 7.47%; found C 72.12%; H 7.59%.

δ_H: 0.94 (6H, t, J 6), 1.28 (3H, s), 1.28–1.52 (8H, m), 1.60–1.72 (6H, m), 1.81 (2H, quintet, J 6), 3.45 (2H, s), 3.48 (2H, t, J 6), 4.03 (2H, t, J 6), 4.36 (2H, d, J 6), 4.46 (2H, d, J 6), 5.16 (1H, quintet, J 6), 7.01 (2H, d, J 8), 7.39 (1H, t, J 9), 7.64 (2H, d, J 8), 7.75 (2H, d, J 8), 7.88–7.93 (2H, m), 8.23 (2H, d, J 8). ν_{max} (film)/cm^{-1}: 2940, 2870, 1750, 1715, 1605, 1500, 1430, 1255, 1180, 1115, 1060, 1015, 950, 900, 830, 760. m/z: 634 (M$^+$), 382 (100%), 352, 279, 197, 139.

(*R*)-(−)-4-(1-Methylheptyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M4)

The experimental procedure was the same as for the preparation of compound **M1**. The following quantities were used: compound **27**, 1.23 g, 3.1 mmol; compound **18**, 0.83 g, 3.1 mmol; DCC, 0.64 g, 3.1 mmol; DMAP, 0.10 g, 0.1 mmol; dichloromethane, 50 ml. Yield 1.09 g (55%), $[\alpha]_D^{24} = -17.4$ (c 0.00826 in CHCl$_3$); SmC* 63.9 SmA* 77.8 Iso liq. °C. Elemental analysis for $C_{39}H_{49}F_1O_7$: calculated C 72.18%; H 7.62%; found C 71.69%; H 7.48%.

δ_H: 0.88 (3H, t, J 6), 1.24–1.52 (14H, m), 1.31 (3H, s), 1.38 (3H, d, J 6), 1.65 (2H, quintet, J 6), 1.83 (2H, quintet, J 6), 3.35 (2H, s), 3.36 (2H, t, J 6), 4.02 (2H, t, J 6), 4.35 (2H, d, J 6), 4.52 (2H, d, J 6), 5.18 (1H, sextet, J 6), 7.01 (2H, d, J 8), 7.09–7.15 (2H, m), 7.60 (2H, d, J 8), 7.69 (2H, d, J 8), 8.01 (1H, t, J 9), 8.22 (2H, d, J 8). ν_{max} (film)/cm^{-1}: 2940, 2870, 1740, 1710, 1610, 1520, 1500, 1430, 1250, 1195, 1140, 1060, 1020, 930, 870, 735, 700. m/z: 648 (M$^+$), 381 (100%), 351, 278, 197, 139, 55.

(*S*)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M5)

The experimental procedure was the same as for the preparation of compound **M1**. The following quantities were used: compound **27**, 1.31 g, 3.30 mmol; compound **19**, 0.75 g, 3.30 mmol; DCC, 0.68 g, 3.30 mmol; DMAP, 0.10 g, 0.10 mmol; dichloromethane, 50 ml. Yield 1.24 g (62%), $[\alpha]_D^{24} = +2.3$ (*c* 0.02627 in $CHCl_3$); K 60.4 SmC* 123.6 SmA* 140.5 Iso liq. °C. Elemental analysis for $C_{36}H_{43}F_1O_7$: calculated C 71.25%; H 7.15%; found C 71.02%; H 7.04%.

δ_H: 0.96 (3H, t, *J* 6), 1.02 (3H, d, *J* 6), 1.31 (3H, s), 1.41–1.50 (6H, m), 1.63 (2H, sextet, *J* 6), 1.83 (3H, octet, *J* 6; sextet, *J* 6), 3.48 (2H, s), 3.49 (2H, t, *J* 6), 4.02 (2H, t, *J* 6), 4.20 (2H, m), 4.35 (2H, d, *J* 6), 4.51 (2H, d, *J* 6), 7.01 (2H, d, *J* 8), 7.10–7.15 (2H, m), 7.60 (2H, d, *J* 8), 7.71 (2H, d, *J* 8), 8.04 (1H, t, *J* 9), 8.22 (2H, d, *J* 8). ν_{max} (KBr disc)/cm^{-1}: 2940, 2880, 1730, 1710, 1610, 1530, 1500, 1435, 1300, 1280, 1250, 1190, 1130, 1060, 1020, 970, 900, 830, 770, 725, 700. *m*/*z*: 606 (M$^+$), 381 (100%), 279, 197, 139, 55.

4-(1-Propylbutyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate (M6)

The experimental procedure was the same as for the preparation of compound **M1**. The following quantities were used: compound **27**, 1.25 g, 3.20 mmol; compound **20**, 0.80 g, 3.20 mmol; DCC, 0.67 g, 3.20 mmol; DMAP, 0.10 g, 0.10 mmol; dichloromethane, 50 ml. Yield 1.08 g (54%); K 42.6 (SmA 30.4) Iso liq. °C. Elemental analysis for $C_{38}H_{47}F_1O_7$: calculated C 71.89%; H 7.47%; found C 71.60%; H 7.29%.

δ_H: 0.94 (6H, t, *J* 6), 1.32 (3H, s), 1.40–1.58 (8H, m), 1.59–1.75 (6H, m), 1.83 (2H, quintet, *J* 6), 3.47 (2H, s), 3.48 (2H, t, *J* 6), 4.03 (2H, t, *J* 6), 4.36 (2H, d, *J* 6), 4.53 (2H, d, *J* 6), 5.20 (1H, quintet, *J* 6), 7.01 (2H, d, *J* 8), 7.08–7.15 (2H, m), 7.60 (2H, d, *J* 8), 7.71 (2H, d, *J* 8), 8.04 (1H, t, *J* 9), 8.21 (2H, d, *J* 8). ν_{max} (film)/cm^{-1}: 2940, 2870, 1740, 1710, 1610, 1530, 1500, 1430, 1280, 1250, 1190, 1120, 1060, 1015, 900, 830, 770, 700. *m*/*z*: 634 (M$^+$), 520, 382, 352, 197, 139, 55 (100%).

Poly{(*R*)-(−)-4-(1-methylheptyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P1)[‡]

Compound **M1** (0.800 g, 1.230 mmol) and photoinitiator (SARCAT KI 85) (0.021 g, 2 mol%, 0.025 mmol) were dissolved in dichloromethane (approx. 5 ml) and pipetted onto a sheet of glass over an area of 190 cm^2 (19 × 10 cm). The solvent was evaporated off in an oven (80 °C) over 30 minutes. The polymerisation mixture was then sandwiched by a second sheet of glass and cooled to room temperature under nitrogen and with exclusion of light. The polymerisation mixture was exposed to UV light for 1 h with cooling (a N_2 gas stream cooled by liquid nitrogen) and then cured in an oven (80 °C) for 1 h. The polymer was then cooled to room temperature and dissolved in dichloromethane (approx. 250 ml) and washed with water (150 ml). The organic solution was then dried (Na_2SO_4). The drying agent was filtered off and the solvent removed *in vacuo* to yield the crude polymer which was purified by precipitation from dichloromethane with hexane. This precipitation process was repeated 3 times to ensure removal of all unreacted monomer. The polymer was then dissolved in dichloromethane and filtered through a 0.45 μm filter. The solvent was removed *in vacuo* and the polymer dried *in vacuo* (P_2O_5). Yield 0.260 g (33%), $[\alpha]_D^{25} = -20.1$ (*c* 0.00416 in $CHCl_3$); T_g 10.3 SmC* 127.9 SmA* 147.6 Iso liq. °C.

δ_H (CD_2Cl_2): 0.87 (3H, br t), 0.92 (3H, s), 1.23–1.34 (12H, br m), 1.34–1.63 (7H, br m), 1.65–1.82 (2H, br m), 3.21 (4H, s), 3.25 (2H, s), 3.36 (2H, br t), 3.93 (2H, br t), 5.11 (1H, br sextet), 6.93 (2H, br d), 7.33 (1H, br t), 7.55 (2H, br d), 7.65 (2H, br d), 7.86 (2H, br m), 8.16 (2H, br d).

Poly{(*S*)-(+)-4-(2-methylbutyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P2)

The experimental procedure was the same as for the preparation of compound **P1**. The following quantities were used: compound **M2**, 0.800 g, 1.320 mmol; SARCAT KI 85, 0.022 g, 2 mol%, 0.026 mmol. Yield 0.500 g (63%), $[\alpha]_D^{24} = +3.5$ (*c* 0.00683 in $CHCl_3$); T_g 1.9 SmX* 161.5 SmC* 178.7 SmA* 192.7 Iso liq. °C.

δ_H (CD_2Cl_2): 0.91 (3H, s), 0.94 (3H, d, *J* 6), 0.99 (3H, t, *J* 6), 1.21–1.32 (2H, br m), 1.36–1.60 (6H, br m), 1.73–1.88 (3H, br m), 3.21 (4H, s), 3.25 (2H, s), 3.35 (2H, br t), 3.92 (2H, br t), 4.14 (2H, m), 6.91 (2H, d, *J* 8), 7.31 (1H, t, *J* 8), 7.52 (2H, d, *J* 8), 7.63 (2H, d, *J* 8), 7.80–7.90 (2H, m), 8.13 (2H, d, *J* 8).

Poly{4-(1-propylbutyloxycarbonyl)-2-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P3)

The experimental procedure was the same as for the preparation of compound **P1**. The following quantities were used: compound **M3**, 0.800 g, 1.260 mmol; SARCAT KI 85, 0.021 g, 2 mol%, 0.025 mmol. Yield 0.600 g (75%); T_g 10.5 SmC 94.3 Iso liq. °C.

δ_H (CD_2Cl_2): 0.92 (9H, br m), 1.30–1.50 (8H, br m), 1.50–1.70 (6H, br m), 1.72–1.82 (2H, br m), 3.22 (4H, s), 3.25 (2H, s), 3.36 (2H, br t), 3.93 (2H, br t), 5.15 (1H, br quintet), 6.93 (2H, br d), 7.33 (1H, br t), 7.54 (2H, br d), 7.65 (2H, br d), 7.87 (2H, br m), 8.16 (2H, br d).

Poly{(*R*)-(−)-4-(1-methylheptyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P4)

The experimental procedure was the same as for the preparation of compound **P1**. The following quantities were used: compound **M4**, 0.800 g, 1.230 mmol; SARCAT KI 85, 0.021 g, 2 mol%, 0.025 mmol. Yield 0.430 g (52%), $[\alpha]_D^{24} = -16.8$ (*c* 0.00997 in $CHCl_3$); T_g −0.3 SmC* 123.1 SmA* 137.3 Iso liq. °C.

δ_H (CD_2Cl_2): 0.88 (3H, br t), 0.93 (3H, s), 1.23–1.35 (13H, br m), 1.35–1.65 (6H, br m), 1.70–1.84 (2H, m), 3.23 (4H, s), 3.25 (2H, s), 3.38 (2H, br t), 3.98 (2H, t), 5.15 (1H, br sextet), 6.97 (2H, br d), 7.05–7.15 (2H, br m), 7.58 (2H, br d), 7.72 (2H, br d), 8.00 (1H, br t), 8.18 (2H, br d).

Poly{(*S*)-(+)-4-(2-methylbutyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P5)

The experimental procedure was the same as for the preparation of compound **P1**. The following quantities were used: compound **M5**, 0.800 g, 1.320 mmol; SARCAT KI 85, 0.022 g, 2 mol%, 0.026 mmol. Yield 0.520 g (65%), $[\alpha]_D^{24} = +1.2$ (*c* 0.00999 in $CHCl_3$); T_g 0.8 SmC* 190.1 SmA* 222.2 Iso liq. °C.

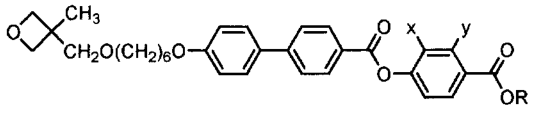
δ_H (CD_2Cl_2): 0.91 (3H, s), 0.93 (3H, d, *J* 6), 0.96 (3H, t, *J* 6), 1.19–1.31 (2H, m), 1.33–1.59 (6H, br m), 1.69–1.89 (3H, br m), 3.20 (4H, s), 3.23 (2H, s), 3.36 (2H, br t), 3.97 (2H, br t), 4.14 (2H, m), 6.95 (2H, br d), 7.03–7.18 (2H, br m), 7.56 (2H, br d), 7.68 (2H, br d), 7.99 (1H, br t), 8.15 (2H, br d).

Poly{4-(1-propylbutyloxycarbonyl)-3-fluorophenyl 4′-[6-(3-methyloxetan-3-ylmethoxy)hexyloxy]biphenyl-4-carboxylate} (P6)

The experimental procedure was the same as for the preparation of compound **P1**. The following quantities were used: compound **M6**, 0.800 g, 1.260 mmol; SARCAT KI 85, 0.021 g, 2 mol%, 0.025 mmol. Yield 0.250 g (30%); SmC 165.4 SmA 185.6 Iso liq. °C.

[‡] The IUPAC names for polymers **P1**–**P6** are poly(oxy{2-methyl[2-(6-{4′-[4-alkoxycarbonyl-2- or -3-fluorophenoxycarbonyl]biphenyl-4-yloxy}hexyloxymethyl]trimethylene}).

Table 1 Transition temperatures (°C) and enthalpies of transition (J g^{-1}) for monomers **M1**–**M6** and the parent monomers **I**–**III**



Compound no.	R	x	y	Mp[a]/°C ($\Delta H_{transition}$/J g^{-1})	Iso liq.	Transition temperature/°C	BPI		BPIII		N*		SmA/ SmA*		SmC/ SmC*		SmX*	Recryst[a]
I	1-MH*	H	H	34.5 (24.2)	•	102.1 (4.0)	—	—	—	—	—	—	•	58.3 (0.2)	•	—	—	<−70
II	2-MB*	H	H	36.6 (24.5)	•	134.1 (4.6)	•	130.7	—	—	—	—	•	90.6 (0.2)	•	[13.3 (0.2)	•][b]	<−70
III	1-PB	H	H	35.7 (34.6)	•	64.9 (3.1)	—	—	—	—	—	—	•	49.5 (0.2)	•	—	—	<−70
M1	1-MH*	F	H	<−70	•	61.6 (2.0)	—	—	—	—	—	—	•	40.0 (0.1)	•	—	—	<−70
M2	2-MB*	F	H	0.8 (9.8)	•	99.0 (0.4)[c]	—	—	•	95.5 (0.4)[c]	•	89.6 (1.2)	•	51.9 (<0.1)	•	—	—	<−70
M3	1-PB	F	H	<−70	•	10.3 (0.7)	—	—	—	—	—	—	—	—	•	—	—	<−70
M4	1-MH*	H	F	<−70	•	77.8 (2.0)	—	—	—	—	—	—	•	63.9 (0.5)	•	—	—	<−70
M5	2-MB*	H	F	60.4 (56.3)	•	140.5 (4.9)	—	—	—	—	—	—	•	123.6 (<0.1)	•	—	—	<−70
M6	1-PB	H	F	42.6 (3.2)	•	[30.4 (0.3)	—	—	—	—	—	—	•]	—	—	—	—	<−70

[a] The melting points and the recrystallisation temperatures were determined by DSC. [b] Transition in square brackets shows a monotropic transition. [c] The enthalpy values for the BPIII and N* transition are combined due to overlapping peaks.

δ_H (CD_2Cl_2): 0.91 (3H, s), 0.94 (6H, br t), 1.25–1.47 (6H, br m), 1.47–1.72 (8H, br m), 1.75–1.84 (2H, m), 3.20 (4H, s), 3.23 (2H, s), 3.34 (2H, br t), 3.90 (2H, br t), 5.17 (1H, br quintet), 6.97 (2H, br d), 7.09–7.18 (2H, br m), 7.58 (2H, br d), 7.68 (2H, br d), 8.02 (1H, br t), 8.19 (2H, br d).

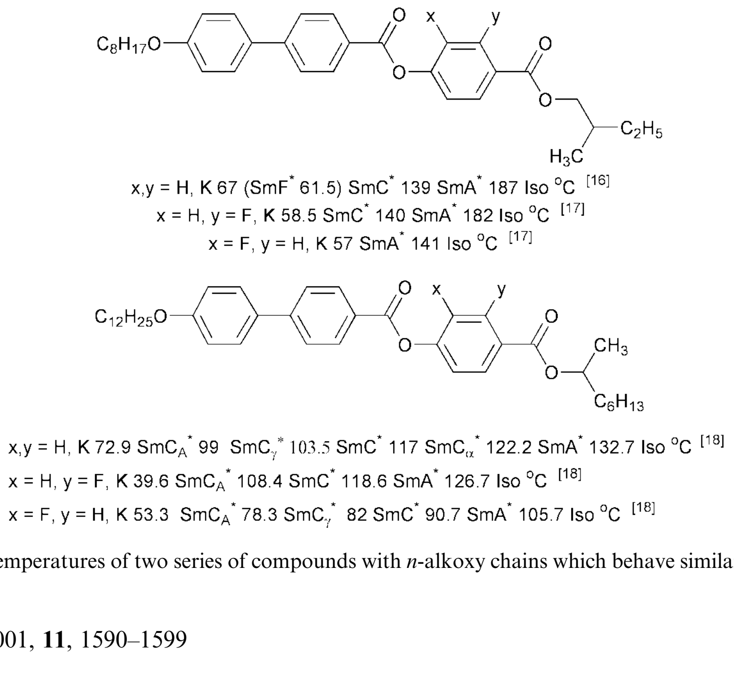
Results and discussion

Mesomorphic behaviour of the monomers

The transition temperatures for compounds **M1**–**M6** and the analogous parent systems, **I**–**III**,[9] are given in Table 1. Monomers **M1**–**M6** are all mesogenic with the 3-fluoro compounds (**M4**–**M6**) generally showing higher melting points than the 2-fluoro analogues (**M1**–**M3**) (however, it should be noted that a melting point could not be detected for **M4**). Similarly, where comparisons are possible, the mesophase stabilities of the 3-fluoro compounds are higher than for the 2-fluoro analogues.

Monomers **M1**, **M2**, **M4** and **M5** were all found to exhibit SmA* and SmC* phases, and the monomers with the achiral 1-propylbutyl chain gave either SmC (**M3**) or SmA (**M6**) phases. Monomer **M2** is particularly interesting because, not only does it have a low melting point of 0.8 °C and exhibits SmA* and SmC* phases, it is the only compound in the series to show BPIII and a chiral nematic phase.

Comparisons of the transition temperatures for the monomers synthesised in these studies with those of the parent analogues, **I**–**III**, show some interesting differences related to the effect of either the 2- or the 3-fluoro substitution. For the 2-fluoro compounds, there is, without exception, a reduction in mesophase stabilities and melting points in comparison with those obtained for the parents (compare **I** and **M1**; **II** and **M2**; and **III** and **M3**); the reductions range from 18.3 to 41.1 °C with greater relative reductions for the smectic A* phase.



x,y = H, K 67 (SmF* 61.5) SmC* 139 SmA* 187 Iso °C [16]

x = H, y = F, K 58.5 SmC* 140 SmA* 182 Iso °C [17]

x = F, y = H, K 57 SmA* 141 Iso °C [17]

x,y = H, K 72.9 SmC_A* 99 SmC_γ* 103.5 SmC* 117 SmC_α* 122.2 SmA* 132.7 Iso °C [18]

x = H, y = F, K 39.6 SmC_A* 108.4 SmC* 118.6 SmA* 126.7 Iso °C [18]

x = F, y = H, K 53.3 SmC_A* 78.3 SmC_γ* 82 SmC* 90.7 SmA* 105.7 Iso °C [18]

Fig. 2 Structure and transition temperatures of two series of compounds with *n*-alkoxy chains which behave similarly to compounds **I**–**III** and **M1**–**M6**.

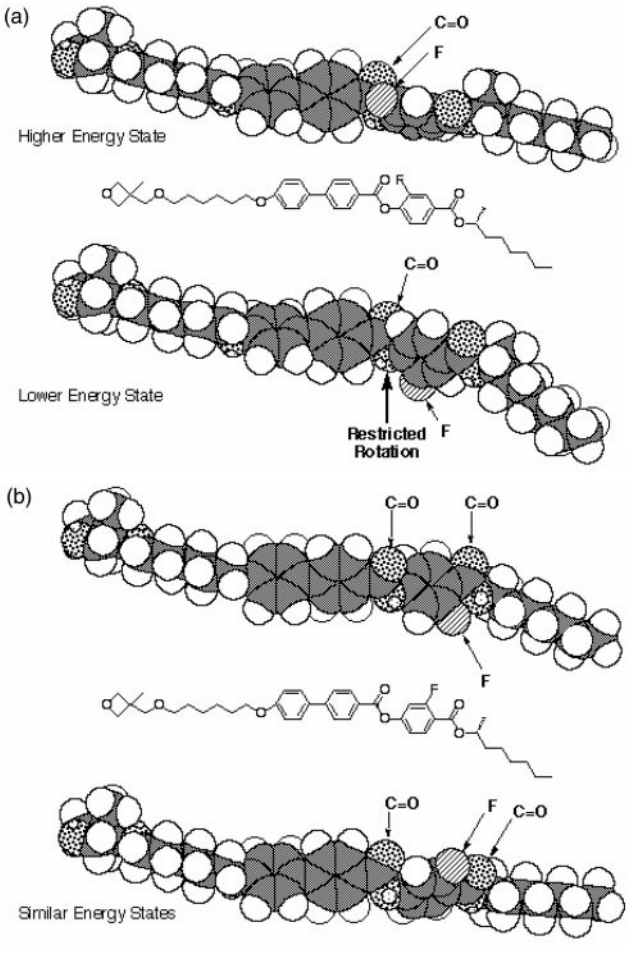


Fig. 3 (a) The minimised space filling molecular structure of **M1**, (b) the minimised space filling molecular structure of **M4**.

The introduction of a 3-fluoro substituent into the mesogenic core gives a much less coherent picture with respect to property–structure correlations. For the following pairs of analogues, **II** and **M5** and **III** and **M6**, the 3-fluoro materials have higher melting points, but for **I** and **M4** the melting point of the 3-fluoro monomer is significantly lower. The patterns for the changes in mesophase stabilities are also somewhat erratic; comparison between **III** and **M6** shows a reduction in smectic A stability, **I** and **M4** shows an increase in smectic C* and a decrease in smectic A* stabilities, and **II** and **M5** shows an increase in both smectic C* and A* stabilities so that the clearing point for **M5** is higher than for **II**. Thus, the overall results and the differences between the two fluoro systems are consistent with those found for some similar *n*-alkoxy compounds, see Fig. 2.

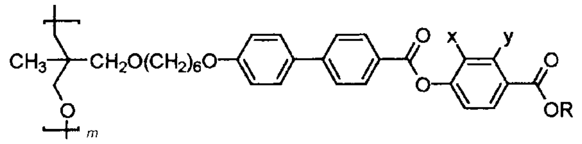
The similarity of the transition temperatures of the 3-fluoro compounds with those of the parents can be attributed to the space-filling of the fluorine atom but, more importantly by maintaining the linearity of the core, allowing the molecules to pack in such a way as to encourage the formation of the lamellar type ordering that is required for smectic phase formation. The 2-fluoro systems have reduced transition temperatures compared to the parent system and this might be attributed to the interaction of the fluorine atom and the inner carbonyl of the ester group. The interaction between the fluorine and the carbonyl may be a repulsive interaction, causing an internal twist in the core which depresses smectic phase formation. Indeed, modelling of the 2-fluoro and 3-fluoro substituted 1-methylheptyl esters **M1** and **M4** shows that the rotation about the central ester linkage is severely restricted for the 2-fluoro analogue in comparison to the 3-fluoro material. The restricted rotation has the effect of positioning the carbonyl moiety of the central ester group (for a good portion of its time) on the opposing side of the molecule to the 2-fluoro substituent, see Fig. 3(a). This leads to the possibility of the dipoles associated with the carbonyl group and the fluoro substituent opposing one another. The opposing strongly polar groups located at the heart of the central core of the 2-fluoro materials probably lead to reduced lateral interactions of the molecules thereby resulting in reduced stability of the smectic state in comparison to the 3-fluoro analogues (Fig. 3(b)).

Mesomorphism and molecular weight of the polymers

The polymerisation of the monomers occurred in varying yields, but typically the polymers were obtained in yields >50%, with polymers **P1** (33%) and **P6** (30%) as the exceptions. Table 2 summarises the molecular weight results determined by GPC analysis and shows that the monomers **M1**–**M3** give polymers of higher DP than monomers **M4**–**M6**. This suggests that the termination rate is faster for polymerisation of compounds **M4**–**M6** which have the 3-fluoro substituent. Polymers **P1**–**P3** have higher molecular weights than **P4**–**P6** but they also have greater degrees of polydispersity.

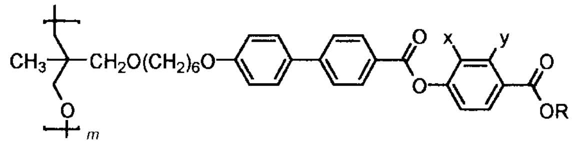
The transition temperatures for polymers **P1**–**P6** and the parent polymers **PI**–**PIII** are shown in Table 3. All of the polymers exhibit smectic C/C* phases which are typically exhibited over a very wide temperature range, *e.g.*, from below room temperature up to 190.1 °C for **P5**, and the phases which arise for the polymers are almost precisely the same as those

Table 2 Molecular weight and DP values of polymers **P1**–**P6** and polymers **PI**–**PIII** determined by GPC



Compound No	R	x	y	M_n	M_w	M_w/M_n	DP
PI	1-MH*	H	H	14575	30449	2.0	23
PII	2-MB*	H	H	10998	21497	2.0	19
PIII	1-PB	H	H	13700	20674	1.5	22
P1	1-MH*	F	H	9122	14052	1.5	14
P2	2-MB*	F	H	13757	30550	2.2	23
P3	1-PB	F	H	9828	16734	1.7	16
P4	1-MH*	H	F	7121	9393	1.3	11
P5	2-MB*	H	F	5074	7058	1.3	9
P6	1-PB	H	F	5131	6096	1.2	8

Table 3 Transition temperatures (°C) and enthalpies of transition (J g^{-1}) for polymers **P1**–**P6** and the parent polymers **PI**–**PIII**



				Transition temperature/°C ($\Delta H_{\mathrm{transition}}$/J g^{-1})							
Compound no.	R	x	y	Iso liq.		SmA/SmA*		SmC/SmC*		SmX*	T_g[a]
PI	1-MH*	H	H	●	167.8 (1.7)	●	150.2 (0.3)	●	—	—	11.8
PII	2-MB*	H	H	●	227.8 (9.2)	●	190.3 (<0.1)	●	—	—	19.0
PIII	1-PB	H	H	●	146.5 (5.0)	●	134.5 (0.1)	●	—	—	11.2
P1	1-MH*	F	H	●	147.6 (5.5)	●	127.9[b]	●	—	—	10.3
P2	2-MB*	F	H	●	192.7 (6.5)	●	178.7 (0.1)	●	161.5 (0.3)	●	1.9
P3	1-PB	F	H	●	94.3 (2.9)	—	—	●	—	—	10.5
P4	1-MH*	H	F	●	137.3 (1.3)	●	123.1 (0.6)	●	—	—	−0.3
P5	2-MB*	H	F	●	222.2 (4.1)	●	190.1 (0.4)	●	—	—	0.8
P6	1-PB	H	F	●	185.6 (0.5)	●	165.4 (<0.1)	●	—	—	—

[a]Determined by DSC. [b]No enthalpy value determined because the transition occurs as a shoulder on a very broad SmA*–Iso liq. transition.

found for the monomers; the only exceptions being that the nematic phase of **M2** is suppressed for the polymer, and a smectic C phase was induced for polymer **P6**.

Polymer **P2** exhibited an unidentified mesophase below the SmC* phase; the textures of both the SmC* phase and the SmX* phase are shown in Fig. 4. The SmX* phase can be confirmed as being a tilted phase because a *schlieren* texture is observed, however, the *schlieren* brushes are small and are difficult to focus upon; typically the bulk of the texture of the smectic phase of the polymer tends to be made up of focal–conic domains.

On examination of the DSC results, a small peak (0.3 J g^{-1}) representing the SmC*–SmX* transition was observed which was larger than the SmA*–SmC* transition (0.1 J g^{-1}). As a result it is inconclusive whether the SmX* phase is an antiferroelectric SmC$_A$* phase or a higher ordered smectic phase, such as smectic I*.

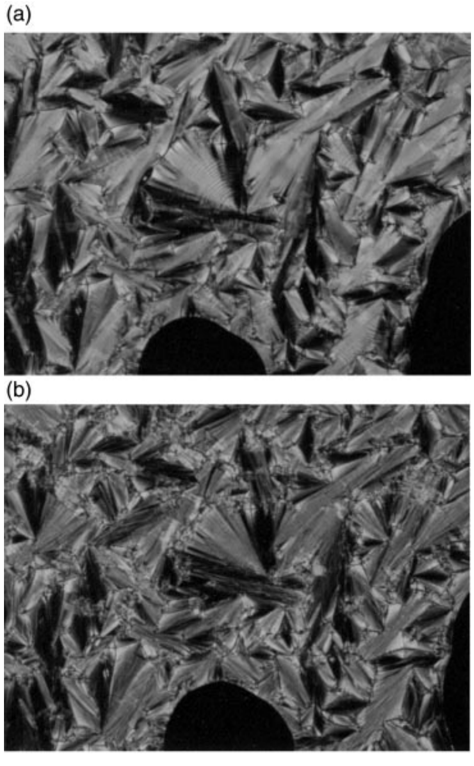


Fig. 4 Photomicrographs of the textures of **P2**; (a) SmC* phase at 178 °C, (b) SmX* at 161 °C.[1]†

Comparison of polymers **P3** and **P6** shows that **P3** has a higher clearing point than **P6**, whereas for the monomers, **M3** had a lower clearing point than **M6**. This observation can be attributed to the difference in the DP values of the polymers; **P3** has a DP value double that of **P6**. One of the most important points that can be made about all of the polymers is that during microscopy, very little annealing time is required to obtain a well-defined defect texture. Typically, the annealing time to create a defect texture, of the type normally exhibited by low molar mass materials, is about 5 minutes compared to the few hours or maybe longer required for structurally similar acrylates or polysiloxanes (often these systems only produce poorly defined, sandy textures). The polymer textures that are shown in Fig. 4 for **P2**, a polymer with a DP of 23, arise after annealing in the SmA* phase for five minutes, 5 °C below the clearing point.

The T_g values for all the polymers are low, and lie within the range −0.3 to 10.5 °C, and for **P6** a T_g value could not be detected.

Comparison of the results for the polymers in this work with those for the polymers with the parent core (see Table 2) shows that DP values for **P1**–**P3** are similar to those for **PI**–**PIII**, except in the case of **P2** which has a DP value 4 units higher. The transition temperatures for all of the polymers with a 2-fluoro substituent (**P1**–**P3**) are much lower than for the parent polymers and the T_g values are also lower. **P4** exhibits transition temperatures which are comparable with **P1**, but the transition temperatures of **P5** are similar to those of the parent system, which is quite remarkable especially as the DP value is approximately 10 units lower that **PII**. Polymer **P6** is the only fluoro-substituted polymer from those presented which exhibits transition temperatures that are at higher temperatures compared to the analogous parent system (**PIII**). This increase of transition temperatures is most unexpected since **P6** has the lowest DP of all of the presented polymers, being approximately 14 units lower than **PIII**; all other examples show reduced transition temperatures compared to the parent system.

Conclusion

In this article we have reported the synthesis of two series of liquid-crystalline monomers with oxetane terminal groups and their resulting polymerisation to give side-chain liquid crystalline polymers. The monomeric materials exhibit both smectic A/A* and smectic C/C* mesophases which are preserved upon polymerisation. The polymers formed are of low viscosity as indicated by their ability to anneal quickly and to give excellent mesophase textures seen through optical microscopy.

The series of monomers (**M4**–**M6**) and polymers (**P4**–**P6**) with a 3-fluoro substituent, in some cases, show superior liquid crystal properties with respect to the parent systems, particularly with respect to the smectic C/C* temperature ranges, while the materials which incorporate a 2-fluoro substituent show reduced smectic C/C* stabilities. All of the monomers have low melting points, and the polymers show low T_g values. The suitability of these materials for potential applications is being assessed by measuring their electrooptical properties (P_s, tilt angles and response times).

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