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Synthesis and SmC* properties of chiral liquid crystalline terephthalates

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Chiral ester derivatives of terephthalic acid containing one, three, or five phenyl rings were prepared by using (*S*)-2-methylbutanol or (*R*)-2-chloropropanol as starting materials. The one-ring terephthalates did not exhibit any liquid crystalline phases, but one of them was used as a chiral dopant in ferroelectric mixtures. Elongation of the aromatic core structure to three and five phenyl rings stabilized the SmA phase, whereas a (monotropic) SmC* phase was detected in some three-ring and five-ring derivatives. In ferroelectric mixtures based on the terephthalates, spontaneous polarizations up to 340 $\mathrm{nC\,cm^{-2}}$ were measured.

1. Introduction

The liquid crystalline properties of terephthalic acid derivatives consisting of three *para*-phenyl rings have been investigated rather extensively in the past [1–6]. Attention has usually been devoted to terephthalate esters with achiral alkylphenyl or alkoxyphenyl residues, which were also taken as low molar mass model compounds for thermotropic liquid crystalline polyesters based on the corresponding phenyl terephthalate mesogenic units [7, 8]. However, reports concerned with chiral liquid crystalline terephthalates [5, 9] and the ferroelectric properties of their SmC* mesophases have been rather few. In this respect, one should note that chiral one-ring terephthalic acid derivatives have been examined as dopants for inducing chirality and ferroelectricity in achiral SmC mixtures [10–12]. To the best of our knowledge, no chiral five-ring terephthalic acid derivatives have so far been described.

In this paper we report on the synthesis of some chiral one-, three- and five-ring terephthalates and their liquid crystalline properties, either as single compounds or as components of ferroelectric mixtures.

2. Experimental

2.1. *Methods*

Infrared spectra were taken with a NICOLET MAGNA 750 FTIR spectrometer using KBr pellets and/or solutions (CCl_4, $CHCl_3$). The thickness of the KBr cell used was 0·01 cm, and the resolution was 4 $\mathrm{cm^{-1}}$. If it was necessary, overlapping νC=O bands were resolved with Fourier Self-Deconvolution (FSD). Nuclear magnetic resonance (^{1}H NMR) spectra were taken with a VARIAN

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XL-400 MHz spectrometer at 25°C; the chemical shifts (δ) are referred to the internal standard tetramethylsilane. ^{1}H assignments were obtained with the aid of homonuclear spin decoupling and evaluated according to figure 1. Mass spectra were taken with a KRATOS MS-80 instrument with the following settings: EI ionization, 70 eV, trap current 100 μA, direct introduction, 200°C. CI ionization 100 eV, isobutane reagent gas; direct introduction, 230°C.

Optical microscopy studies were carried out with an AMPLIVAL pol-u polarizing microscope equipped with a Boetius hot stage. The textures of liquid crystal mixtures were observed in thin film form between glass slides using polarized light with crossed polarizers. The phase transition temperatures were determined by polarizing microscopy and by differential scanning calorimetry under a flow of dry nitrogen using a Mettler TA3000 apparatus. The temperature scale was calibrated against the melting temperature of indium. The transition temperatures were taken from the heating traces as corresponding to the onset point of the enthalpic peaks at a heating rate of 2 K min^{-1}.

Optical rotation data were measured with a POLAMAT A polarimeter, using various solvents.

2.2. *Materials*

(*S*)-2-methylbutanol (**2a**) and (*S*)-ethyl lactate were purchased from Aldrich. 4-Ethoxycarbonyloxybenzoic acid (**4**), (*R*)-2-chloropropanol (**2b**) [13], (*R*)-2-chloropropyl 4-ethoxycarbonyloxybenzoate [13], (*S*)-2-methylbutyl 4-hydroxybenzoate (**5a**) [14], 4-(2-methylbutyl)phenol (**10**) [15, 16], and (*R*)-2-chloropropyl 4-hydroxybenzoate (**5b**) [13] have been described earlier.

2.2.1. *(R)-bis-2-chloropropyl terephthalate (**3b**)*

Terephthaloyl chloride (**1**) (2·3 g, 11 mmol) was reacted with (*R*)-2-chloropropanol (**2b**) (2·15 g, 23 mmol) in the presence of triethylamine (2·32 g, 23 mmol) in 30 ml of dry benzene at 0°C. After one day's stirring, the reaction mixture was poured into iced water and the organic layer washed with 5% aqueous HCl, water, 5% aqueous $NaHCO_3$ and water, and dried over $MgSO_4$. The crude product obtained after evaporation was crystallized from ethanol: 2·2 g (yield 64%), m.p. 100–101°C, $[\alpha]_D^{22\cdot 5} = +39\cdot 57$ ($c = 5\cdot 0$ ethyl acetate). IR (KBr): 2987–2870 ($\nu C_{Al}H$), 1721 ($\nu C{=}O$), 1504 ($\nu C_{Ar}C_{Ar}$), 1280 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR ($CDCl_3$): 1·61 (d, 6H, 2 × CH_3), 4·33 (m, 2H, 2 × CHCl), 4·46 (d, 4H, 2 × OCH_2), 8·14 (s, 4H, C2-H, C3-H, C5-H, C6-H). MS *m/z*: 283 (M–Cl; 0·5%), 225 (100%), 167 (40%) 149 (50%), 04 (30%), 76 (50%). $C_{12}H_{16}Cl_2O_4 = 319$.

2.2.2. *(S)-4-(2-methylbutyloxycarbonyl)phenyl 4-(ethoxycarbonyloxy)benzoate (**7a**)*

4-Ethoxycarbonyloxybenzoyl chloride (**6**) (4·57 g, 20 mmol) was reacted under cooling with (*S*)-2-methylbutyl 4-hydroxybenzoate (**5a**) (4·16 g, 20 mmol) in the presence of dry pyridine (1·6 g, 20 mmol) in anhydrous benzene (40 ml). After stirring overnight at room temperature, the reaction mixture was heated under reflux for 30 min. After cooling, the reaction mixture was poured into water and the organic layer washed with 5% aqueous HCl, water, 5% aqueous $NaHCO_3$ and water, and dried over $MgSO_4$. Yield after evaporation and recrystallization from absolute ethanol was 5·0 g (62%) of **7a**, m.p. 53–54°C, $[\alpha]_D^{24\cdot 0} = +4\cdot 0$ ($c = 1\cdot 0$ $CHCl_3$). IR (KBr): 3069 ($\nu C_{Ar}H$), 2966–2877 ($\nu C_{Al}H$), 1763, 1741, 1713 ($\nu C{=}O$), 1601, 1509 ($\nu C_{Ar}C_{Ar}$), 1270 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR ($CDCl_3$): 0·97 (t, 3H, CH_3), 1·03 (d, 3H, CH_3), 1·3 + 1·53 (m, 2H, CH_2), 1·4 (t, 3H, CH_3), 1·88 (m, 1H, CH), 4·16 + 4·22 (dd, 2H, OCH_2), 4·37 (q, 2H, OCH_2), 7·30 (m, 2H, C3-H + C5-H), 7·37 (m, 2H, C3′-H + C5′-H), 8·12 (m, 2H, C2-H + C6-H), 8·24 (m, 2H, C2′-H + C6′-H). MS *m/z*: 400 (M; 0·1%), 313 (5%), 193 (100%), 121 (80%). $C_{22}H_{24}O_7 = 400$.

2.2.3. *(S)-4-(2-methylbutyloxycarbonyl)phenyl 4-hydroxybenzoate (**8a**)*

(*S*)-4-(2-methylbutyloxycarbonyl)phenyl 4-ethoxycarbonyloxybenzoate (**7a**) (3 g, 7·5 mmol) was dissolved in ethanol (15 ml) and ethyl acetate (3 ml) and cooled to +5°C under constant stirring; 25% aqueous ammonium hydroxide (22·6 ml) was added dropwise to the solution. The reaction was monitored by TLC. After complete removal of the protecting group, the reaction mixture was neutralized under cooling with 20% aqueous HCl, and ethyl acetate (30 ml) was added to the solution. The organic layer was separated, washed with 5% aqueous $NaHCO_3$ and water, dried over $MgSO_4$ and evaporated. The oil obtained solidified under hexane. After recrystallization from benzene : cyclohexane (1 : 1), 1·2 g (yield 49%) of **8a** was obtained as white needles, m.p. 87–88°C, $[\alpha]_D^{20\cdot 0} = +3\cdot 47$ ($c = 5\cdot 0$ ethyl acetate). IR (KBr): 3304 (νOH), 3081, 3068 ($\nu C_{Ar}H$), 2963–2877 ($\nu C_{Al}H$), 1735, 1689 ($\nu C{=}O$), 1608, 1593, 1516 ($\nu C_{Ar}C_{Ar}$) 1264 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR ($CDCl_3$): 0·96 (t, 3H, CH_3),

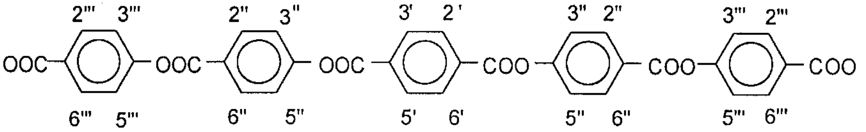


Figure 1. Assignment of chemical shifts in ^{1}H NMR spectra.

1·03 (d, 3H, CH_3), 1·30 + 1·52 (m, 2H, CH_2), 1·87 (m, 1H, CH), 4·13 + 4·22 (dd, 2H, OCH_2), 5·94 (s, 1H, OH), 6·92 (m, 2H, C3-H + C5-H), 7·30 (m, 2H, C′-H + C5′-H), 8·11 (m, 4H, C2-H + C6-H + C2′-H + C6′-H). MS *m/z*: 328 (M; 1%), 241 (3%), 121 (100%). $C_{19}H_{20}O_5 = 328$.

2.2.4. *(S)-bis-4-(2-methylbutyloxycarbonyl)phenyl terephthalate (**9a**)*

$[\alpha]_D^{24\cdot0} = +6\cdot0$ ($c = 5\cdot0$ benzene). IR (CCl_4): 2966–2878 ($\nu C_{Al}H$), 1747, 1723 (νC=O), 1605, 1502 ($\nu C_{Ar}C_{Ar}$), 1260, 1190 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR ($CDCl_3$): 0·98 (t, 6H, 2 × CH_3), 1·04 (d, 6H, 2 × CH_3), 1·30 + 1·54 (m, 4H, 2 × CH_2), 1·88 (m, 2H, 2 × CH), 4·16 + 4·23 (dd, 4H, 2 × OCH_2), 7·35 (m, 4H, 2 × C3″-H + 2 × C5″-H), 8·16 (m, 4H, 2 × C2″-H + 2 × C6″-H), 8·35 (s, 4H, C2′-H, C3′-H, C5′-H, C6′-H). MS *m/z*: 546 (M; 0·2%), 459 (0·5%), 339 (100%), 121 (20%), 104 (35%). $C_{32}H_{34}O_8 = 546$.

2.2.5. *(S)-bis-{4-[4-(2-methylbutyloxycarbonyl)phenyl]-oxycarbonyl}phenyl terephthalate (**12a**)*

$[\alpha]_D^{24\cdot0} = +0\cdot3$ ($c = 1\cdot0$ dioxane). IR ($CHCl_3$): 2946–2878 ($\nu C_{Al}H$), 1743, 1726, 1715 (νC=O), 1603, 1579, 1505 ($\nu C_{Ar}C_{Ar}$), 1259 cm^{-1} (ν_{as}–O–C–(O)–C). ^{1}H NMR ($CDCl_3$): 0·97 (t, 6H, 2 × CH_3) 1·04 (d, 6H, 2 × CH_3), 1·28 + 1·58 (m, 4H, 2 × CH_2), 1·88 (m, 2H, 2 × CH), 4·15 + 4·23 (dd, 4H, 2 × OCH_2), 7·32 (m, 4H, 2 × (C3‴-H + C5‴-H)), 7·45 (m, 4H, 2 × (C3″-H + C5″-H)), 8·15 (m, 4H, 2 × (C2‴-H + C6‴-H)), 8·33 (m, 4H, 2 × (C2″-H + C6″-H)), 8·39 (s, 4H, C2′-H, C3′-H, C5′-H, C6′-H). MS *m/z*: 786 (M; <0·1%), 699 (3%), 579 (100%), 459 (30%), 339 (20%), 121 (100%). $C_{46}H_{42}O_{12} = 786$.

2.2.6. *(R)(S)-bis-4-(2-methylbutyl)phenyl terephthalate (**11**)*

IR (KBr): 3040 ($\nu C_{Ar}H$), 2963–2854 ($\nu C_{Al}H$), 1731 (νC=O), 1605, 1509 ($\nu C_{Ar}C_{Ar}$), 1272 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR: 0·92 (t, 6H, 2 × CH_3), 0·87 (d, 6H, 2 × CH_3), 1·2–1·45 (m, 4H, 2 × CH_2), 2·35–2·70 (dd, 4H, 2 × CH_2), 1·65 (m, 2H, 2 × CH), 7·13 (m, 4H, 2 × C3″-H + 2 × C5″-H), 7·21 (m, 4H, 2 × C2″-H + 2 × C6″-H), 8·30 (s, 4H, C2′-H, C3′-H, C5′-H, C6′-H). MS *m/z*: 458 (M; 7%), 295 (100%), 121 (25%), 104 (35%). $C_{30}H_{34}O_4 = 458$.

2.2.7. *(R)-4-(2-chloropropoxycarbonyl)phenyl 4-ethoxycarbonyloxybenzoate (**7b**)*

4-Ethoxycarbonyloxybenzoyl chloride (**6**) (1·4 g, 6·2 mmol) was added dropwise to a solution of (*R*)-2-chloropropyl 4-hydroxybenzoate (**5b**) (1.33 g, 6·2 mmol) in dry benzene (30 ml) and pyridine (1·6 g, 20 mmol) at +5°C. After 24 h at room temperature, water (30 ml) was added and the organic layer was washed with 5% aqueous HCl, water, 5% aqueous Na_2CO_3, water, dried over $MgSO_4$ and evaporated to dryness. After recrystallization from ethanol 1·5 g (yield 61%) of **7b** was obtained, m.p. 60–62°C, $[\alpha]_D^{20\cdot8} = -15\cdot15$ ($c = 1\cdot0$ $CHCl_3$). IR (KBr): 3082 ($\nu C_{Ar}H$), 2989–2872 ($\nu C_{Al}H$), 1766, 1744, 1736 (νC=O), 1603, 1508 ($\nu C_{Ar}C_{Ar}$), 1267 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR: 1·61 (d, 3H, CH_3), 1·41 (t, 3H, CH_3), 4·32 (m, 1H, CH), 4·36 (q, 2H, CH_2), 4·44 (d, 2H, OCH_2), 7·32 (m, 2H, C3-H + C5-H), 7·36 (m, 2H, C3′-H + C5′-H), 8·16 (m, 2H, C2-H + C6-H), 8·24 (m, 2H, C3′-H + C6′-H). MS *m/z*: 406 (M; 0·1%), 371 (0·1%), 313 (5%), 193 (75%), 121 (100%). $C_{20}H_{19}ClO_7 = 406\cdot5$.

2.2.8. *(R)-4-(2-chloropropoxycarbonyl)phenyl 4-hydroxybenzoate (**8b**)*

M.p. 136–138°C, $[\alpha]_D^{24\cdot0} = -12\cdot80$ ($c = 1\cdot0$ $CHCl_3$). IR (KBr): 3395 (νOH), 1722, 1705 (νC=O), 1606, 1591, 1512 ($\nu C_{Ar}C_{Ar}$), 1274 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR: 1·61 (d, 3H, CH_3), 4·32 (m, 1H, CH), 4·44 (d, 2H, OCH_2), 5·7 (bs, 1H, OH), 6·92 (m, 2H, C3-H, C5-H), 7·31 (m, 2H, C3′-H + C5′-H), 8·12 (m, 2H, C2-H + C6-H), 8·16 (m, 2H, C2′-H + C6′-H). MS *m/z*: 334 (M; 0·2%), 241 (4%), 138 (4%), 121 (100%). $C_{17}H_{15}ClO_5 = 334\cdot5$.

2.2.9. *(R)-bis-4-(2-chloropropoxycarbonyl)phenyl terephthalate (**9b**)*

Terephthaloyl chloride (**1**) (1·0 g, 5 mmol) was suspended in dry benzene (40 ml) and (*R*)-2-chloropropyl 4-hydroxybenzoate (**5b**) (2·1 g, 10 mmol) and triethylamine (2·0 g, 20 mmol) were added under cooling. After stirring overnight, the reaction mixture was poured into water; the organic layer was washed with 5% aqueous HCl, water, 5% aqueous $NaHCO_3$, water, dried over $MgSO_4$ and evaporated. The crude product was recrystallized from ethanol or ethyl acetate–petroleum ether. $[\alpha]_D^{26\cdot0} = -15\cdot68$ ($c = 0\cdot516$ $CHCl_3$). IR (CCl_4): 2990, 2935 ($\nu C_{Al}H$), 1748, 1730 (νC=O), 1605, 1501 ($\nu C_{Ar}C_{Ar}$) 1259 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR: 1·62 (d, 6H, 2 × CH_3), 4·34 (m, 2H, 2 × CH), 4·45 (d, 4H, 2 × OCH_2), 7·37 (m, 4H, 2 × C3″-H + 2 × C5″-H), 8·18 (m, 4H, 2 × C2″-H + C6″-H + C6″-H), 8·34 (s, 4H, C2-H, C3-H, C5-H, C6-H). MS CI: *m/z*: 561 (M + H; 100%), EI: *m/z*: 465 (8%), 345 (100%), 121 (40%), 104 (50%). $C_{28}H_{24}Cl_2O_8 = 559$.

2.2.10. *(R)-bis-{4-[4-(2-chloropropoxycarbonyl)phenyl]-oxycarbonyl}phenyl terephthalate (**12b**)*

$[\alpha]_D^{24\cdot0} = -9\cdot10$ ($c = 0\cdot185$ dioxane). IR (KBr): 3067 ($\nu C_{Ar}H$), 2972–2882 ($\nu C_{Al}H$), 1737, 1727, 1715 (with FSD) (νC=O), 1602, 1507 ($\nu C_{Ar}C_{Ar}$), 1268 cm^{-1} (ν_{as}–O–C(O)–C). ^{1}H NMR ($CDCl_3$): 1·65 (d, 6H, 2 × CH_3), 4·34 (m, 2H, 2 × CH), 4·46 (d, 4H, 2 × OCH_2), 7·36 (m, 4H, 2 × (C3‴-H + C5‴-H)), 7·46 (m, 4H,

$2\times(C3''-H+C5''-H)$), 8·19 (m, 4H, $2\times(C2'''-H+C6'''-H)$), 8·32 (m, 4H, $2\times(C2''-H+C6''-H)$), 8·40 (s, 4H, C2′-H, C3′-H, C5′-H, C6′-H). MS *m/z*: 798 (M; <0·1%), 705 (3%), 585 (40%), 465 (18%), 343 (10%), 121 (100%). $C_{42}H_{32}Cl_2O_{12}=799$.

3. Results and discussion

3.1. *Synthesis*

In the synthesis of the terephthalates we have applied three different esterification reactions, namely direct ester formation, coupling by dicyclohexylcarbodiimide (DCC) and condensation via an acid chloride (figure 2). The one-ring derivatives **3a** and **3b** were synthesized by reacting terephthaloyl chloride (**1**) with the appropriate optically active alcohol **2a** and **2b**, respectively.

(*S*)-2-Methylbutyl 4-hydroxybenzoate (**5a**) was prepared by acid catalysed direct ester formation without appreciable racemization [14], whereas the same reaction for the preparation of the 2-chloropropyl analogue occurred with complete racemization, as described earlier [13]. In contrast, (*R*)-2-chloropropyl 4-hydroxybenzoate (**5b**) was easily prepared by first reacting 4-ethoxycarbonyloxybenzoyl chloride (**6**) with (*R*)-2-chloropropanol under mild conditions, and then cleaving the protecting group by rapid ammonolysis. **5a** and **5b** were finally coupled with **1** thus giving the chiral three-ring terephthalates **9a** and **9b**. Another three-ring derivative, bis 4-(2-methylbutyl)phenyl terephthalate (**11**), was prepared by coupling 4-(2-methylbutyl)phenol (**10**) [15, 16] with **1**.

The aromatic core structure of **5a** and **5b** was elongated by reacting them with **6** to give compounds **7a** and **7b** which were then deprotected by ammonolysis leading to (*S*)-4-(2-methylbutyloxycarbonyl)phenyl 4-hydroxybenzoate (**8a**) and (*R*)-4-(2-chloropropoxycarbonyl)-phenyl 4-hydroxybenzoate (**8b**), the key intermediates of the five-ring terephthalates **12a** and **12b**.

The one-ring derivatives **3a** and **3b** do not exhibit any liquid crystalline phase, as expected. Comparing the properties of the three-ring liquid crystalline terephthalates, one can see that the racemic compound **11** forms only a nematic phase, while both **9a** and **9b** (table 1) have SmC*, SmA*, N* and blue phases. Compound **9b** suffers some thermal decomposition at temperatures close to the clearing point. The five-ring derivative **12a** exhibits enantiotropic SmA*, N* and two different blue phases, while **12b** forms enantiotropic N* and monotropic SmA* and SmC* phases (table 1). Therefore, the elongation of the aromatic core structure of the terephthalates favours stabilization of the SmA* and blue phase for **9a**, **9b**, whereas the SmC* phase is monotropic in **9a**, **9b** and enantiotropic in **12b**.

3.2. *Studies on ferroelectric mixtures*

Many aspects of the molecular framework of SmC* liquid crystal materials have been taken into consideration for the understanding and tuning of the ferroelectric properties of single compounds and mixtures [17]. We have extended the considerations described in [17] to our ferroelectric mixtures to understand the appearance or disappearance of SmC* phases and the effect on the spontaneous polarization.

We have used compounds **13**–**16** as hosts for our terephthalates; these have very different mesophase behaviours (table 2). Both (*S*)-4-(2-methylbutyloxycarbonyl)phenyl 4-*n*-octyloxybenzoate (**14**) [17] and (*S*)-4-(1-cyano-2-methylpropoxycarbonyl)phenyl 4′-(6-hexenyloxy)-biphenyl-4-carboxylate (**15**) [18] form a SmC* phase, which is monotropic at ambient temperature in the former and enantiotropic at high temperature in the latter case. The spontaneous polarization of compound **15** reaches a value as high as $540\,\mathrm{nC\,cm^{-2}}$ [18]. By contrast, (*S*)-bis-1-methylheptyl 1,1′-4′1″-terphenyl-1,4″dicarboxylate (**16**) [19] is not liquid crystalline, while achiral 4-*n*-hexyloxyphenyl 4-*n*-decyloxybenzoate (**13**) exhibits enantiotropic SmC, SmA, N and monotropic SmB phases [20].

Compound **3b** was used as representative of one-ring guests in two kinds of binary mixtures (table 3). Mixture **M1**, obtained by mixing **3b** in low concentration with the host **13**, exhibits a SmC* phase. At higher guest concentrations, the SmC* phase disappeared. Mixture **M2** or **3b** with **14** forms a SmC* phase around room temperature; this vanished when the guest was at greater concentrations than 2·19 wt %. Therefore, the non-liquid crystalline dopant **3b** markedly destabilizes the monotropic SmC* phase of the host material. If we consider only that the absolute configuration of the chiral centre in **14** is (*S*) and that the guest material **3b** is (*R*), we can understand this effect. If we take into account that the chiral centre is four atomic bonds away from the core in both molecules, and that the inductive effect is also of opposite sense [17], we would expect that the helix induced by the guest will not destroy the helix of the host. But the experiments showed the opposite. We have to take into account the geometry of the molecules as well.

Three-ring terephthalate **9a** was also used as a dopant in ferroelectric mixtures (table 3). It was mixed with **15** producing binary mixture **M3**, and also with **15** and **16** in different proportions giving ternary mixtures **M4** and **M5**.

Finally, compound **16** was mixed with **15** to give a new ferroelectric mixture **M6**. This exhibited a SmC* phase over a wide temperature range and gave a higher spontaneous polarization than mixtures **M1**–**M5**. **M5** had the longest switching time in comparison with

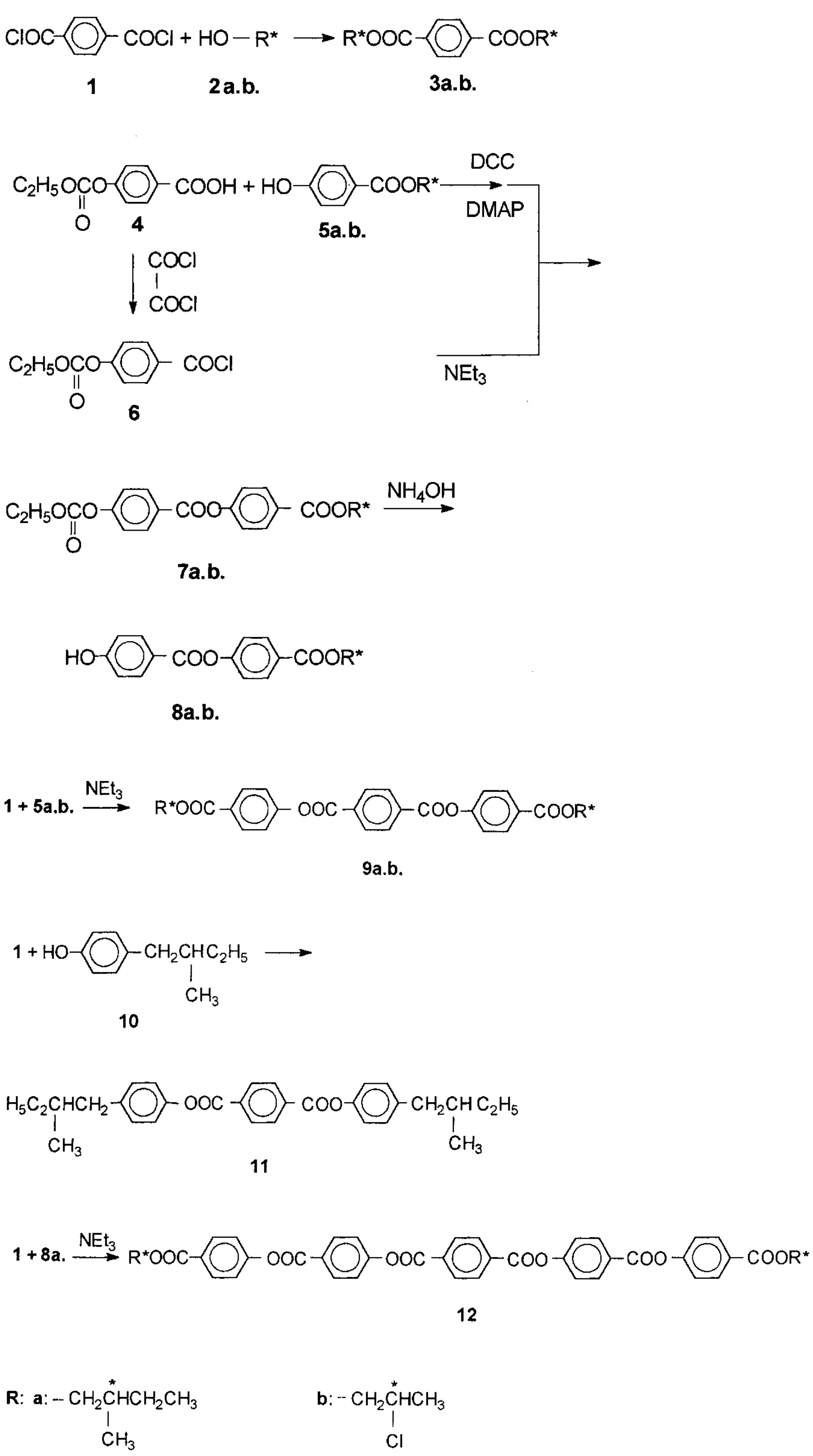
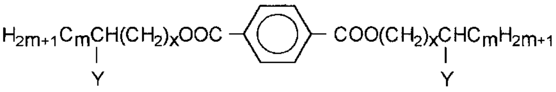


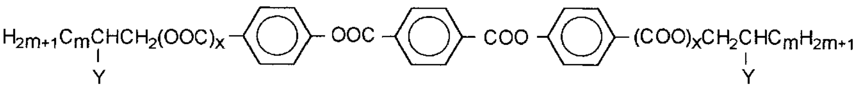
Figure 2. Scheme of synthesis for one-, three- and five-ring terephthalate derivatives.

mixtures **M3** and compound **15** (table 4). The chiral centre of **16** is located three atomic bonds away from the core, and its absolute configuration is (*R*); the inductive effect of the group connected to the chiral centre is (+I). Compound **15** has a high dipole moment on the chiral centre and is of opposite sense (−I), its absolute configuration is (*S*) and the separation of the chiral centre from the core is four atomic bonds.

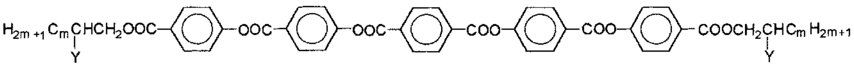
Table 1. Symmetric terephthalates: phase transition temperatures (°C); ( ) denotes monotropic transition.



Compound	*Y*	*m*	*x*	M.p.
3a	CH_3	2	1	oil, b.p. 150/0·08 Hg mm
3b	Cl	1	1	101–2



				Phase sequence				
Compound	*Y*	*m*	*x*	Melting	SmC*–SmA*	SmA*–N*	N*–I	Bp–I
9a	CH_3	2	1	136·5	(112·5)	145·5	159·5	(159·5)
9b	Cl	1	1	152	(117)	(125)	200	(199)
11	CH_3	2	0	110	—	—	132	—



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			Phase sequence		
Compound	*Y*	*m*	Melting	SmC*–N*	N*–I
12a	CH_3	2	220	—	>360
12b	Cl	1	240	256	300 (decomp.)

Table 2. Phase transitions of additives: temperatures are given in °C; ( ) denotes monotropic transition.

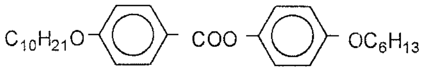
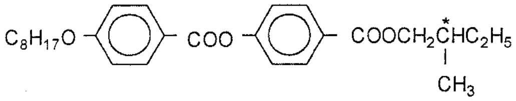
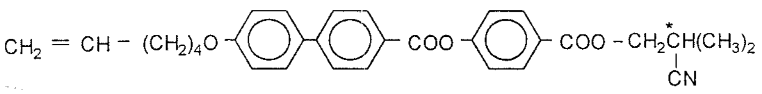
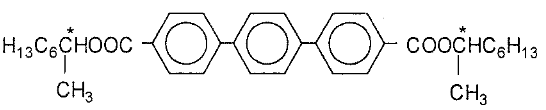
13		Cr (SmB45) 62 SmC 77 SmA 83 N 89I
14		Cr (31SmC*) 34 SmA* 57I
15		Cr (91·2) 116·1 SmC* 145 SmA* 154 N* 156·1I
16		Cr 82I

Table 3. Properties of binary and ternary ferroelectric mixtures: ( ) denotes monotropic transition.

Mixture	Compound	wt %	Phase transitions/°C	$\mathbf{P}_{\mathrm{Smax}}$/nC cm^{-2}
M1	**3b**	4·23	Cr 60 (37 SmB*) SmC* 64 SmA* 75·5 N* 82 I	0·6
	13	95·77		
M2	**3b**	1·40	Cr 34 (24 SmC*) SmA* 55 I	4·2
	14	98·60		
M3	**15**	54·3	Cr 100 SmC* 124 SmA* 147 I	320
	9a	45·7	supercoolable to 58	
M4	**15**	49·4	Cr 87 SmC* 104 SmA* 129–138 I	230
	9a	41·5	supercoolable to 33	
	16	9·1		
M5	**15**	43·4	Cr 80 SmC* 92 SmA* 110–125 I	75
	9a	36·6	supercoolable to 40	
	16	20		
M6	**15**	91·2	Cr 109 SmC* 115 SmA* 139–149 I	340
	16	8·8	supercoolable to 50	

Table 4. Physical parameters of compound **15** and its mixtures.

Material	T_{cryst}/°C	τ/μs^{a} at $\mathbf{E} = 2$ V μm^{-1}
15	93	65
M3	65	30
M5	45	80

[a] Measured 4°C below the SmA*–SmC* transition.

According to [17], as a result, both of them should have a right handed helical structure. However, the spontaneous polarization of **M6**, although high enough [$\mathbf{P}_{\mathrm{S}}$ 340 nC cm^{-2} (table 3)], was smaller than that of compound **15** alone. In this case, probably the molecular geometry and the intermolecular interactions do not allow the maximization of the advantageous properties.

3.3. *Physical properties*

The main physical parameters measured (crystallization temperature, maximum polarization in the SmC* range, and switching time) are summarized in table 4. The pure liquid crystal material **15** had the highest polarization, but also showed the highest crystallization temperature. The ternary mixture **M5** could be cooled down to the lowest temperature, but it had the smallest spontaneous polarization and the longest switching time (table 4). The binary mixture **M3** had the shortest switching time. It is interesting to note that compound **16** [20], which is a chiral dopant inducing high polarization in a non-chiral SmC matrix [18], when used in the ternary mixture **M5** cancels the effect of compound **15** (cell thickness 6 μm, clean glass surfaces).

The spontaneous polarization was determined by measuring the electric current flowing through the sample under a triangular shaped applied voltage. The time dependence of the current is shown for the binary mixture **M3** (polyimide coated 6 μm thick EHC cell, $T = 115{\cdot}4$°C, $f = 4$ Hz) (figure 3). In figure 4 (*a*) the electric current is plotted as a function of the applied voltages for different maximum voltages ($f = 3$ Hz, 108·5°C) for pure **15**. It is seen that there are two peaks (one at negative and one at positive fields). In the curves, the voltage decreases in a linear manner from the maximum positive voltage. As the time derivative of the voltage is increased, the positions of the peaks shift downward, figure 4 (*b*). The areas below the peaks (deducting the linear contribution due to the conductivity) were about equal for every maximum voltage. Similar dependences could also be observed for the mixtures **M3** and **M5**. There the polarization humps did not reach their minima in the negative voltage range, indicating that the dynamics of helix reformation are slow compared to the period of the applied field. This could be due to the lower temperature ranges where the helix nucleation process is slower.

At frequencies above about 20 Hz there was only one polarization peak centred near to zero voltage for all the materials studied. At these frequencies the

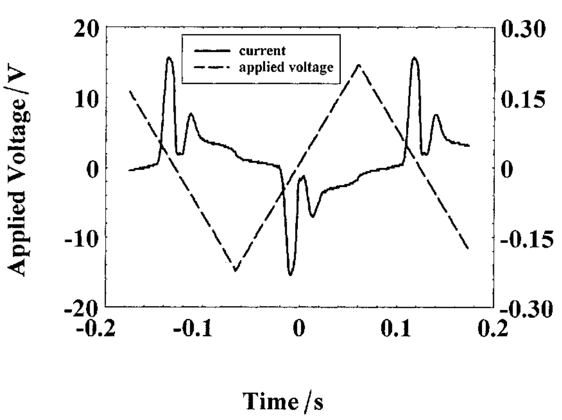
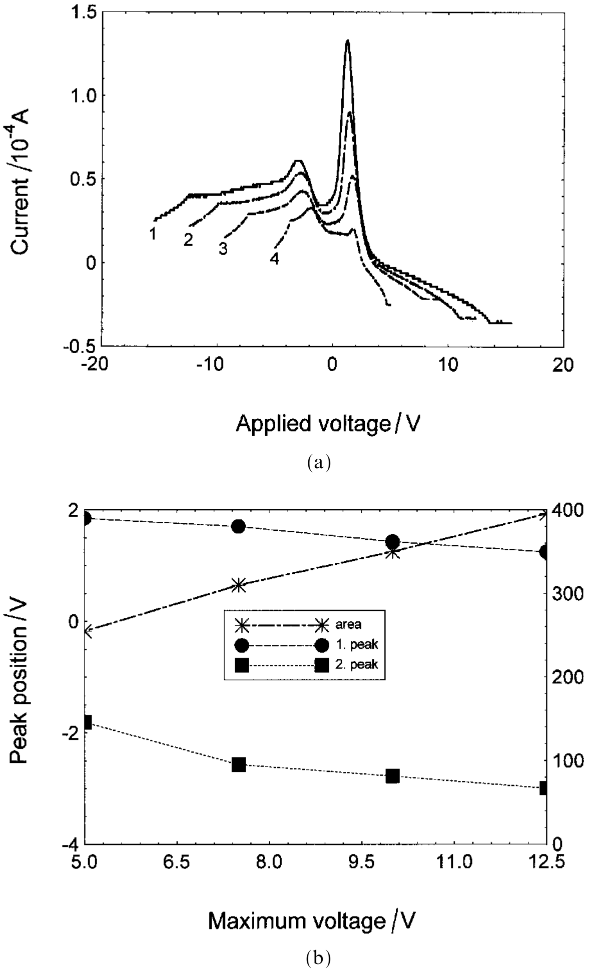


Figure 3. Time dependence of polarization current in mixture **M3**.



(a)

(b)

Figure 4 (*a*). Compound **15**: electric current as a function of applied voltage for maximum voltages of 12·5 V (1), 10 V (2), 7·5 V (3) and 5 V (4). For all curves $f=3$ Hz and $T=108{\cdot}5$°C. It is seen that there are two peaks (one at negative field, the other for positive). (*b*) Peak positions (left axis) and the area below the curves (right axis) with respect to the maximum voltages applied during measurement.

reformation of the alternating (helical ferroelectric or antiferroelectric) structure could not follow the rate of voltage change, and the two peaks overlapped. Such polarization curves could indicate an antiferroelectric structure [21], but could also be the result of helix unwinding and reformation [22]. The polarization current measurements alone are not sufficient to distinguish between the helical ferroelectric and antiferroelectric structures because both produce qualitatively the same time dependences. The value of the polarization was determined from the time integral of the current arising from the reversal of the polarization. The temperature dependences of the polarizations for all the materials studied showed normal behaviour: they increased with decreasing temperatures from zero at T_{AC} to $\mathbf{P}_{max}$ before the onset of crystallization. An example of the temperature dependence of the polarization is shown for binary mixture **M3** (figure 5). The measured data could be fitted over the whole temperature range by the following equation:

$$\mathbf{P}=\mathbf{P}_o(T_{AC}-T)^{\beta} \qquad (1)$$

The best fit is obtained with $\beta=0{\cdot}57$, which is slightly larger than 0·5 as predicted near to T_{AC} by mean field theory [23].

The voltage dependences of the switching time can be fitted by the usual formula [24]:

$$\tau \cong 1{\cdot}8\frac{\gamma}{\mathbf{PE}+Kq^2} \qquad (2)$$

where γ is the rotational viscosity of the sample, $\mathbf{E}$ is the electric field, K is the twist elastic constant, and $q=2\pi/p$, where p is the helical pitch. An example of the voltage dependence of the switching time and the contrast is shown in figure 6 for the binary mixture **M3**. Taking the value of the polarization from figure 5

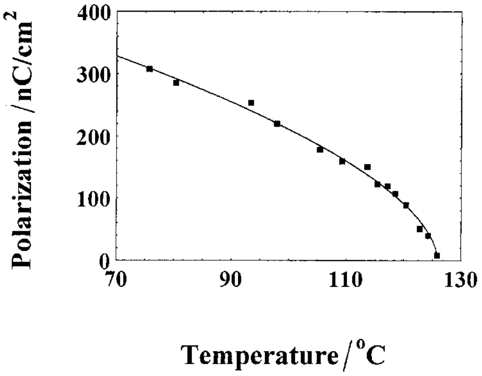


Figure 5. Temperature dependence of polarization of mixture **M3**.

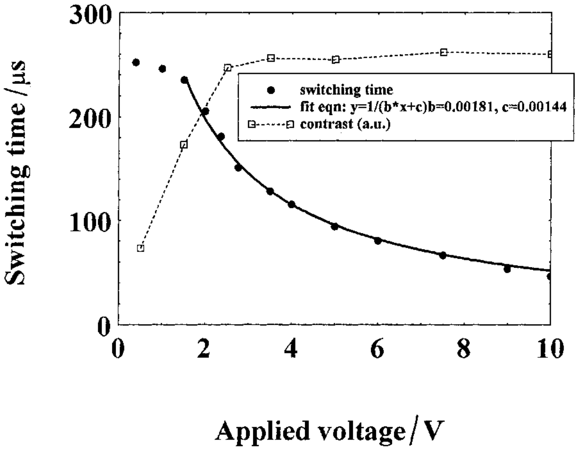


Figure 6. Applied voltage dependence of the switching time and contrast of mixture **M3**.

we find that the rotational viscosity is 0·05 Pa s. The sample appeared greenish in reflected light indicating that $p \sim 0{\cdot}6\,\mu$m. From this we find that the twist elastic constant is 7×10^{-12} N.

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