Fluorescent ferroelectric liquid crystalline copolyacrylates

Alexander Beer[a]; Günter Scherowsky[a]; Hywel Owen[b]; Harry Coles[b]

[a] Institut für Organische Chemie, Berlin, Germany [b] Physics Department, Liquid Crystal Group, University of Manchester, England

PLEASE SCROLL DOWN FOR ARTICLE

Fluorescent ferroelectric liquid crystalline copolyacrylates

by ALEXANDER BEER, GÜNTER SCHEROWSKY*, HYWEL OWEN†
and HARRY COLES†

Institut für Organische Chemie, TU Berlin, 10623 Berlin, Germany
† Physics Department, Liquid Crystal Group, University of Manchester M15 9PL,
England

Fluorescent liquid crystalline side chain polymers were synthesized by copolymerization of a ferroelectric monomer and 5 per cent of various blue fluorescent naphthalic imide dye comonomers. Those copolymers were characterized by DSC, X-ray, GPC and optical microscopy. In favourable cases, fast switching fluorescent ferroelectric polymers resulted, exhibiting high tilt angles (up to $\sim 34°$) and spontaneous polarization values (up to $\sim 115\,nC\,cm^{-2}$) in the S_C^* phase. One fluorescent copolymer shows orthogonal smectic phases exclusively due to the structure of the incorporated fluorescent comonomer. In this case a strong electroclinic effect and high induced tilt angles ($12°$ $10\,V\,\mu m^{-1}$) have been observed in the S_A phase. Order parameters, S, of the dye moieties up to 0.64 were measured in the room temperature S_B phase for the copolymers

1. Introduction

Research on ferroelectric liquid crystalline polymers (FLCP) has been intense over the past few years [1]. In favourable cases FLCP materials allow fast electro-optic switching in the range of some hundred micro-seconds [2, 3]. Due to their viscosity, ferroelectric LC polymers have much better anti-shock characteristics of surface stabilized display devices than those of low molar mass ferroelectric systems. Recently the first flexible FLCP display has been presented based on such structures [4].

Another advantage of polymeric over low molar mass systems is the possibility of combining several functional monomers of different optical or electrical properties through copolymerization. In contrast to mixtures of low molar mass materials, these copolymer systems cannot undergo phase separation due to the linkage of the different components by the polymer backbone. Using this method, a high percentage of dye has been incorporated into nematic polymers [5]. Recently we presented the first examples of coloured FLC copolymers exhibiting bistable electro-optical switching [6].

The guest–host effect of a rod-like azo dye in a nematic LC was discovered some years ago [7]. The use of dichroic dyes in high contrast displays with wide viewing angles is well established [8]. Recently coloured ferroelectric systems have been investigated [9, 10]. Only a few

examples of fluorescent dyes dissolved in ferroelectric materials are known due to their often poor solubility and/or problems with degradation. Nevertheless, suitable dichroic fluorescent dyes could offer advantages over ordinary dyes: large viewing angle (up to 180°), greater brightness and greater perceived contrast [10, 11].

The aim of our work was to incorporate fluorescent dyes into an FLC polymer by copolymerization of a ferroelectric monomer and dichroic fluorescent dye monomers in order to achieve fluorescent FLC copolymers.

Table 1. Structures of the synthesized polymers **15A–D**.
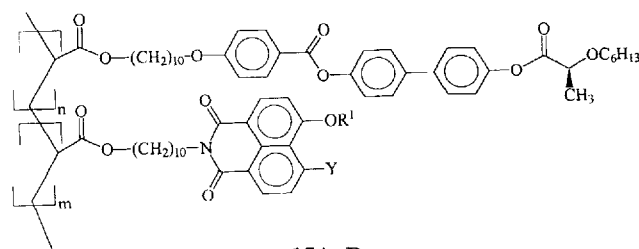
15A–D

Polymer	$n:m/\%$ (w/w)	R^1	Y
15A	$m = 0$	—	—
15B	95:5	CH_3	H
15C	95:5	C_6H_{13}	H
15D	95:5	CH_3	OCH_3

* Author for correspondence.

2. Materials studied

Side chain polyacrylates of the general structure **15** (see table 1) were synthesized and their physical properties investigated. The homopolymer **15A** contains chiral smectogenic side chains exclusively. The copolymers **15B–D** additionally possess fluorescent dye-containing side chains. The basic dye unit is the photochemically and thermally very stable naphthalic imide [12]. This unit was varied in length and number of alkyloxy substituents. Those fluorescent dyes show bright fluorescence in polar solvents and LCs [13]. A statistical distribution of the fluorescent monomer units in the copolyacrylates is assumed due to the preparation process (see below).

3. Preparation of the polyacrylates

The acrylate **11** was prepared in a seven step synthesis (see figure 1): etherification of methyl 4-hydroxybenzoate **1** with 10-bromodecyltetrahydropyranyl ether **2** resulted in the benzoate ester **3**, which was saponified with potassium hydroxide yielding 4-(10-tetrahydropyran-2-yloxy)decyloxybenzoic acid **4**.

Esterification of (*S*)-(−)-2-hexyloxypropanoic acid **5** with 4-hydroxy-4'-benzyloxybiphenyl **6** using the Steglich reaction [14] gave the (*S*)-(−)-2-hexyloxypropionic acid biphenyl ester **7**. Catalytic hydrogenation of the benzylic ether group led to the phenol **8**, which was then esterified with the previously prepared acid **4** resulting in the liquid crytalline compound **9**. Acidic cleavage of the
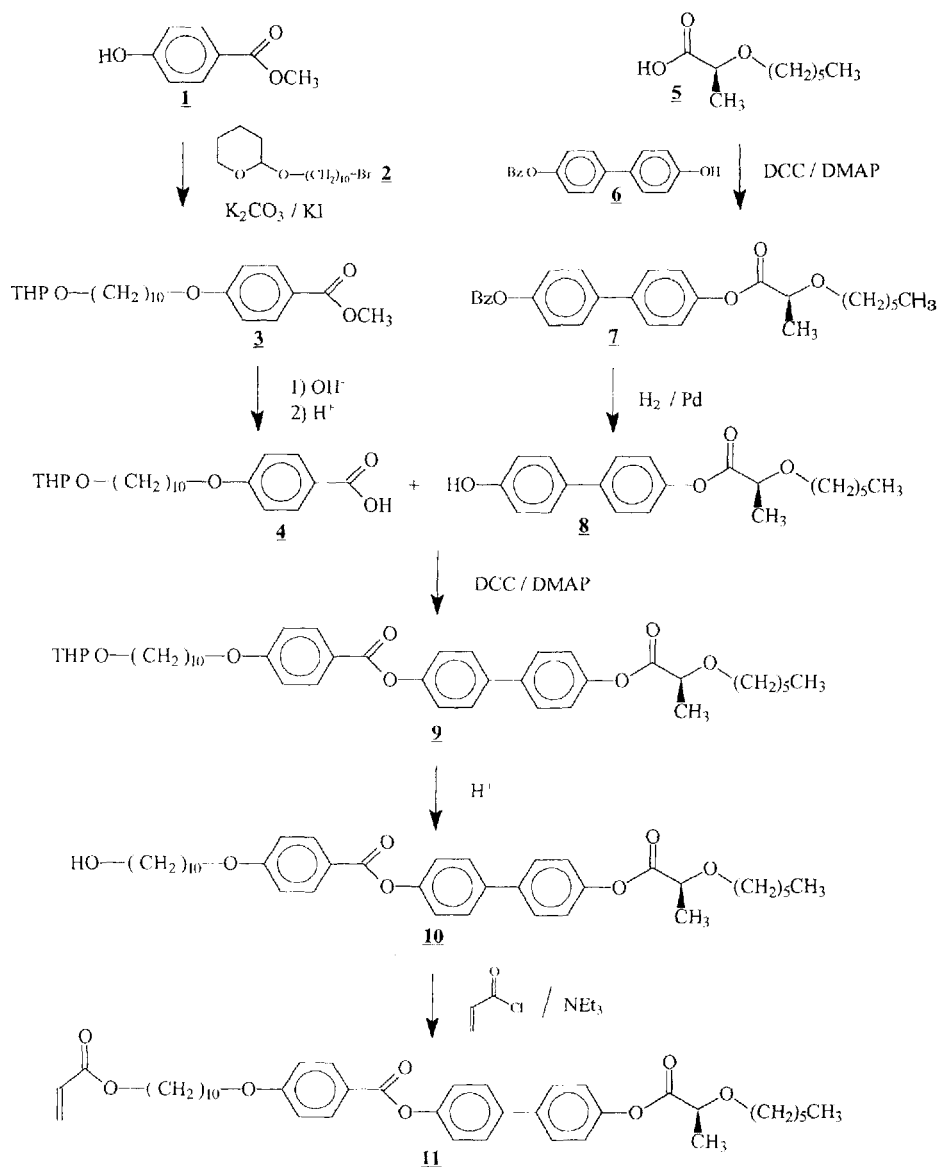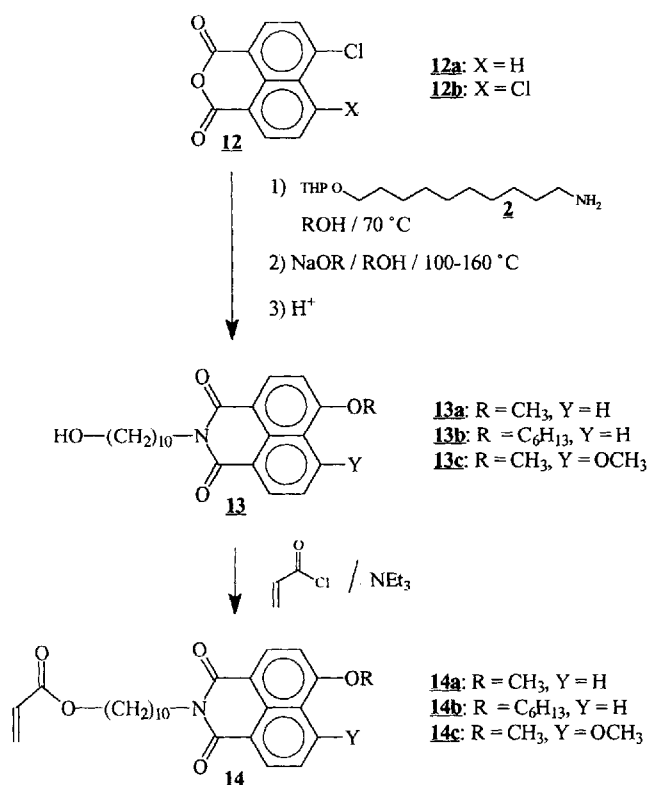

Figure 1. Synthesis of the ferroelectric monomer **11**.

Figure 2. Synthesis of the naphthalic imide dyes 14a–c.

THP ether yielded the 10-hydroxydecyloxybenzoate ester 10, which was esterified with acryloyl chloride/triethylamine to give the ferroelectric monomer 11.

The fluorescent acrylates were synthesized from 4-chloro-1,8-naphthalic acid anhydride 12a or 4,5-dichloro-1,8-naphthalic acid anhydride 12b respectively in a four step procedure (see figure 2, also see [13] for details). In the final step the N-(10-hydroxydecyl)naphthalic imides 13a–c were esterified with acryloyl chloride/triethylamine to give the fluorescent monomers 14a–c.

The polyacrylates 15A–D were prepared from the ferroelectric monomer 11 and the fluorescent monomers 14a–c using the AIBN/toluene system.

4. Physical properties of the polymers

Our LC polymers were characterized by GPC, optical microscopy, DSC, X-ray and electro-optical measure-

ments. From GPC measurements (polystyrene standards), the molar masses M_w of the polymers 15A–C are in the range of $\sim 11\,000$ to $\sim 15\,000$ with polydispersities $D = M_w/M_n$ of approximately 1·5 (see table 2).

The homopolymer 15A exhibits the smectic phases S_B, S_C^* and monotropic S_A (see table 2). The fluorescent copolymers 15B and 15C show the same phase sequence as the homopolymer. The range of the S_C^* phase is about 70 K in both 15A and 15C. In 15B the S_C^* phase range is smaller (57 K) and an enantiotropic S_A phase appears. Copolymer 15D exhibits the orthogonal phases S_B and S_A, but surprisingly no S_C^* phase. This might be due to the more symmetrical dye structure with two methoxy groups where the dye has a tendency to support the formation of orthogonal phases. For this specific dye, we also found this effect in low molar mass ferroelectric mixtures [13].

The polymers were introduced into polyimide coated cells by capillary forces. Homogeneous alignment could be achieved for the copolymers 15B and D using cooling/heating cycles from the isotropic state to room temperature (see figure 3 for textures). The alignment of the polymers 15A and C was more difficult due to their monotropic S_A phase. Therefore the alignment achieved was not completely homogeneous, but good enough to allow optical and electro-optical measurements.

The polymers 15A–C exhibit ferroelectric switching in the S_C^* phase. A comparison of the apparent tilt angles of these polymers is given in figure 4. The homopolymer shows high tilt angles up 37° with the usual behaviour of increasing tilt angles with decreasing temperature. The maximum tilt angles are reduced by the dye side groups in the copolymers to values of 30° (15B) and 34° (15C), respectively.

All the ferroelectric polymers show high values of spontaneous polarization (P_s, see figure 5). As expected the values are lowered in the copolymers (maximum values 15B $\sim 80\,\text{nC}\,\text{cm}^{-2}$, 15C $\sim 115\,\text{nC}\,\text{cm}^{-2}$) with respect to the homopolymer (15A $\sim 150\,\text{nC}\,\text{cm}^{-2}$). Figures 4 and 5 show, that the influence of the dye comonomer strongly depends on its shape: the dye with the short terminal methoxy function (copolymer 15B) reduces both tilt angle and P_s values much further than the terminally elongated hexyloxy dye (copolymer 15C).

The optical response times (10–90 per cent trans-

Table 2. Phase sequences, molar masses and dye order parameters of polymers 15A–D.

Polymer	Mesophases	M_w	M_w/M_n	Order parameter S of the dye moiety
15A	S_B 92 S_C^* (160 S_A) $\sim$ 160 I	10 800	1·48	—
15B	S_B 88 S_C^* 145 S_A $\sim$ 160 I	15 100	1·55	0·49 ± 0·05
15C	S_B 91 S_C^* (158 S_A) $\sim$ 161 I	12 800	1·50	0·53 ± 0·03
15D	S_B 75 S_A $\sim$ 140 I	11 800	1·62	0·64 ± 0·01

(a)

(b)

(e)

(f)

Figure 3. Textures of copolymer **15B** (7·5 μm cell, crossed polarizers, no field applied): (a) homogeneously aligned S_A phase at 147°C, (b) S_C^* phase near to the S_A transition at 143°C, (c) S_C^* phase, defect structure at 95°C, (d) S_B/S_C^* phase transition at 87°C, (e) and (f) ferroelectric switching: (e) bright state at 132°C, $+4·3$ V μm^{-1}, (f) dark state at 132°C, $-4·3$ V μm^{-1}.

Figure 4. Homopolymer **15A** and fluorescent ferrolectric copolymers **15B** and **C**; tilt angles versus temperature.

Figure 5. Homopolymer **15A** and fluorescent ferroelectric copolymers **15B** and **C**; spontaneous polarization versus temperature measured by the current pulse technique.

mission) of the polymers **15A–C** are in the range 10–50 milliseconds (4·3 V μm^{-1}) near to the highly ordered S_B phase and decrease rapidly with increasing temperature to a few hundred microseconds (see figure 6). The incorporated fluorescent dyes give rise to a faster response. The elongated dye (copolymer **15C**) shows the strongest effect in decreasing the response time by about 25 per cent compared to the homopolymer. As an explanation, we assume that incorporation of these dyes reduces the viscosity of the LC polymer, since the spontaneous polarization is lower than for the homopolymer and the tilt angles are similar.
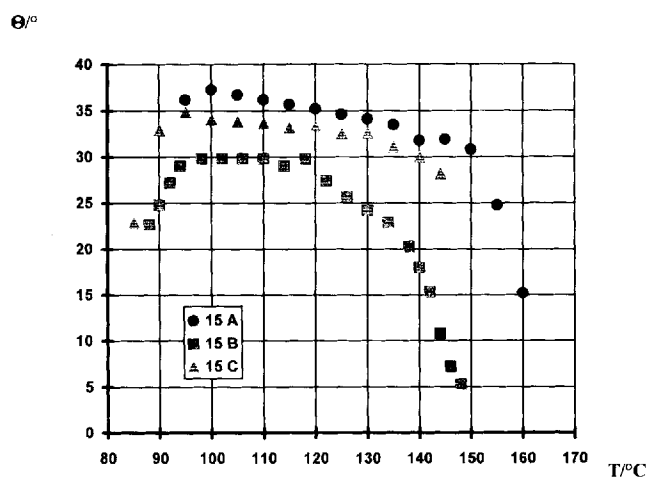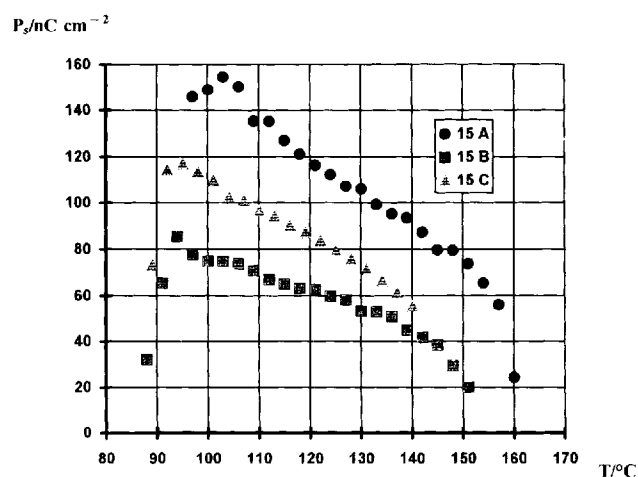
Copolymer **15D** shows a strong electroclinic effect in

the S_A phase. The induced optical tilt angles are linear with respect to the applied field, with high values up to 12° for 10 V μm^{-1} (160 V$_{pp}$, see figure 7). We found fast electro-optic response times between 3 milliseconds near the S_B phase and 400 microseconds near the biphasic region (120°C) (see figure 8).

The order parameter S of the dye moieties in the copolymer systems was measured at room temperature (S_B phase) using the homopolymer as a reference. In highly oriented samples (thickness 4 μm), dye order parameters up to $S = 0·64$ were recorded for copolymer **15D** (see table 2). The apparent order parameters of the dyes in the copolymers **15B–C** are lower due to their transition moment not being parallel to the long axis of the dye molecules.
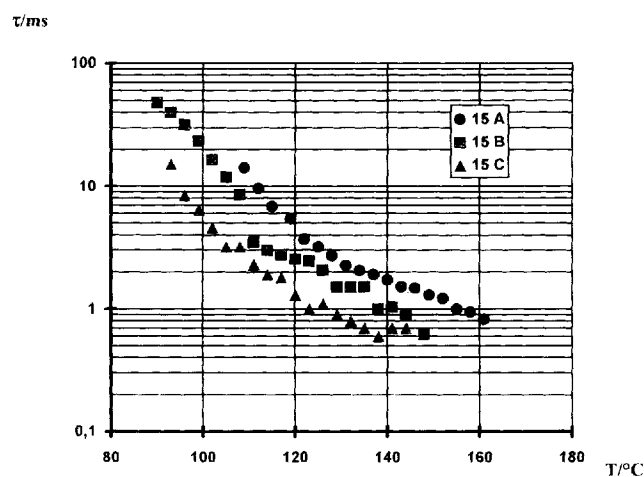
τ/ms

Figure 6.   Homopolymer **15A** and fluorescent ferroelectric copolymers **15B** and **C**; response times versus temperature $(4 \cdot 3 \, \text{V} \, \mu\text{m}^{-1})$ defined as the time for a 10–90 per cent change in transmission.
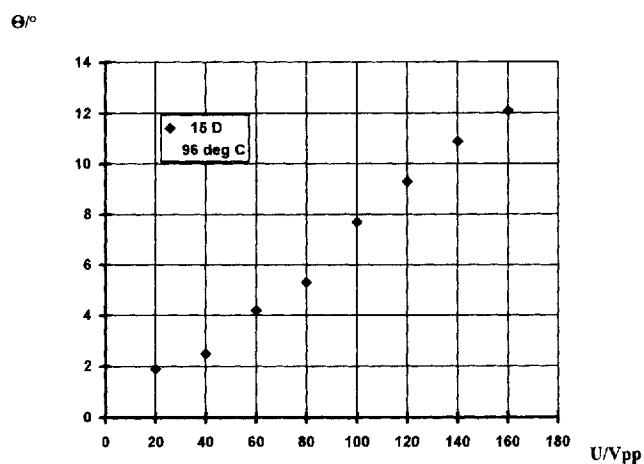
Θ/°

Figure 7.   Fluorescent copolymer **15D**; induced tilt angles versus applied field $(8 \cdot 0 \, \mu\text{m}$ cell).
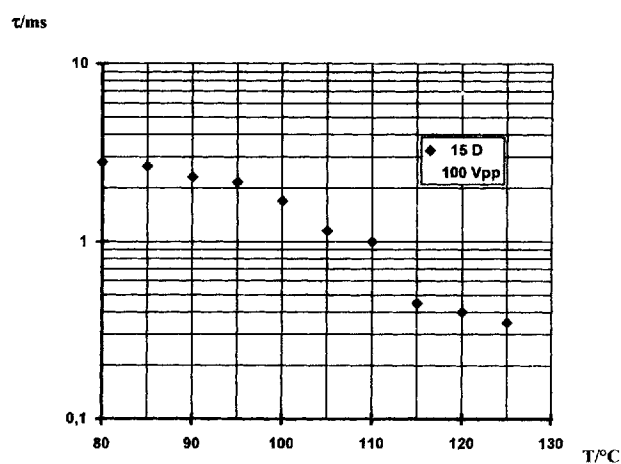
τ/ms

Figure 8.   Fluorescent copolymer **15D**, response times versus temperature.

70 K broad S_C^* phase of the homopolymer completely vanished, being substituted by an electroclinic switching S_A phase in the copolymer. This copolymer exhibits the highest order parameter of the fluorescent dye moiety.

Thus we conclude that fluorescent ferroelectric copolymers have interesting electro-optic properties and that with suitable modifications of the host system, a reduction of the transition temperatures should be possible in order to open the way for applications.

5.   Conclusions

We have synthesized fluorescent ferroelectric copolymers from a new ferroelectric monomer and 5 per cent of a fluorescent dye comonomer. The fluorescent FLC copolymers exhibit broad range S_C^* phases, high tilt angles and high spontaneous polarizations. The influence of the coloured comonomers on the ferroelectric properties of the polymer strongly depends on the dye structure. In one case (**15C**), phase sequence and transition temperatures are almost unchanged in the copolymer with respect to the homopolymer. Tilt angle and P_s values of this copolymer were reduced, but the switching speed was raised.

In an unfavourable case (**15D**), the influence of 5 per cent of the fluorescent comonomer was so strong, that the

6.   Experimental

Instrumental: GPC: PL-gel/solvent THF/polystyrene calibration; X-ray measurements: X-ray generator ISI-DEBYEFLEX 2002/X-ray valve SF 60/monochromator 151 (Huber); DSC: Perkin–Elmer DSC 7/indiums calibration; Melting points and optical microscopy: polarizing microscope Jenapol/hot-stage Linkam THM 600 with TMS 90; Electro-optical measurements: ITO test cells, parallel or antiparallel rubbed PI $(4 \, \mu\text{m}$ or $7\text{–}8 \, \mu\text{m}$ gap)/wave generator Phillips PM 5134/amplifier Krohn–Hite 7500/oscilloscope Gould 1602 with wave form processor/photodiode RS Components BPW 21; Order parameters: spectrophotometer Varian Cary 210; IR spectra: Perkin–Elmer PE 225 and PE 257/solvent $CHCl_3$ if not mentioned; UV spectra: spectrophotometer Beckmann DU-64/solvent $CHCl_3$; Fluorescence spectra: fluorescence spectrophotometer Perkin–Elmer PE 650-60/solvent $CHCl_3$; $[\alpha]_D$ values: polarimeter Perkin–Elmer 141; ^{1}H NMR: 400 MHz Bruker WM 400/solvent $CDCL_3$; MS: Varian MAT 711 and MAT 44 S.

4-(10-tetrahydropyran-2-yloxy)decyloxybenzoate **3** was prepared using standard etherification procedure [6]. Quantities: $2 \cdot 59 \, \text{g}$ (17 mmol) methyl 4-hydroxybenzoate (**1**), $5 \, \text{g}$ ($17 \cdot 3$ mmol) 10-bromo-decyltetrahydropyranyl ether (**2**), $2 \cdot 42 \, \text{g}$ ($17 \cdot 5$ mmol) potassium carbonate and a

pinch of potassium iodide. Yield: 5·2 g (78 per cent), colourless oil. For spectroscopic data see [15].

4-(10-Tetrahydropyran-2-yloxy)decyloxybenzoic acid **4** was prepared using a standard saponification procedure. Quantities: 5·2 g (13·25 mmol) **3** and 1·51 g (27 mmol) potassium hydroxide. Yield; 4·84 g (96·5 per cent), colourless crystals. Phase sequence Cr 81·8 S_X 84·0 I (petroleum ether/ether); for spectroscopic data see [15].

(*S*)-(−)-2-Hexyloxypropanoic acid (4′-benzyloxy-biphenyl-4-yl) ester **7**. A mixture of 2·0 g (11·5 mmol) (*S*)-(−)-hexyloxypropanoic acid (**5**), 3·32 g (12 mmol) 4′-benzyloxy-4-hydroxybiphenyl (**6**), 2·58 g (12·5 mmol) dicyclohexylcarbodiimide (DCC) and 230 mg (1·8 mmol) *N*,*N*-dimethylaminopyridine (DMAP) [14] in 120 ml of dry dichloromethane/10 ml of dry tetrahydrofuran was stirred under an atmosphere of nitrogen for three days at room temperature. The precipitated solid was filtered off and the solution was evaporated. The product was separated by column chromatography (petroleum ether/ dichloromethane (increasing polarity) as eluent). Yield: 3·53 g (71 per cent), crystalline solid. Mp: 115°C (petroleum ether/acetone)), $[\alpha]_D^{21} = -37\cdot4°$ (CHCl$_3$ $c = 1$). IR(KBr) $v = 2933/2861$ (C–H), 1759 (C=O), 1606/1499 (arom.), 814 (1,4-disubst. arom.)cm^{-1}. ^{1}H NMR $\delta = 0\cdot89$, t ($J = 7$ Hz, 3 H); 1·25–1·45, m (6 H); 1·59, d ($J = 7$ Hz, 3 H); 1·67, quint ($J = 7$ Hz, 2 H); 3·50, dt ($J = 9/7$ Hz, 1 H); 3·71, dt ($J = 9/7$ Hz, 1 H); 4·21, q ($J = 7$ Hz, 1 H); 5·11, s (2 H); 7·05/7·50, AA′BB′ ($J = 8\cdot5$ Hz, 4 H); 7·16/7·55, AA′BB′ ($J = 8\cdot5$ Hz, 4 H); 7·35, tt ($J = 7\cdot5/1\cdot5$ Hz, 1 H); 7·41, tt ($J = 7\cdot5/1\cdot5$ Hz, 2 H); 7·47, d (br) ($J = 7\cdot5$ Hz, 2 H); MS (110°C) $m/z = 432$ (14 per cent, M$^+$), 276 (96 per cent, BzOC$_6$H$_4$C$_6$H$_4$O), 91 (100 per cent, C$_6$H$_5$CH$_2$).

(*S*)-(−)-2-Hexyloxypropanoic acid 4′-hydroxy-biphenyl-4-yl ester **8** was prepared using a standard hydrogenation method. Quantities: 3·5 g (8·1 mmol) **7**, 700 mg Pd/C, hydrogen atmosphere. Yield: 2·75 g (99 per cent), crystalline solid. Mp: 106·5°C (ether), $[\alpha]_D^{21} = -43\cdot7°$ (CHCl$_3$, $c = 1$). IR(KBr) $v = 3488$ (H–O), 2935/2862 (C–H), 1735 (C=O), 1610/1501 (arom.), 808 (1,4-disubst. arom.)cm^{-1}. ^{1}H NMR $\delta = 0\cdot89$, t ($J = 7$ Hz, 3 H); 1·26–1·44, m (6 H); 1·59, d ($J = 7$ Hz, 3 H); 1·66, quint ($J = 7$ Hz, 2 H); 3·50, dt ($J = 9/7$ Hz, 1 H); 3·71 dt ($J = 9/7$ Hz, 1 H); 4·21 q ($J = 7$ Hz, 1 H); 4·97, s (OH); 6·87/7·43, AA′BB′ ($J = 8\cdot5$ Hz, 4 H); 7·14/7·52, AA′BB′ ($J = 8\cdot5$ Hz, 4 H). MS (100°C) $m/z = 342$ (5 per cent, M$^+$), 186 (100 per cent, HOC$_6$H$_4$C$_6$H$_4$OH).

(*S*)-(−)-4-(10-Tetrahydropyran-2-yloxydecyloxy)ben-zoic acid [4′-(2-hexyloxypropanoyloxy)biphenyl-4-yl] ester **9** was prepared analogously to **7** using 3·22 g (8·5 mmol) **4**, 2·75 g (8 mmol) **8**, 2·58 g (12·5 mmol) DCC and 170 mg (1·4 mmol) DMAP. Yield: 3·80 g (68 per cent), crystalline solid. Phase sequence Cr ∼ 30 S_X 55 N* 84·0 I (dichloromethane/petroleum ether), $[\alpha]_D^{21} = -24\cdot2°$

(CHCL$_3$, $c = 1$). IR(KBr) $v = 2930/2854$ (C–H), 1773 (C=O), 1733 C=O), 1607/1495 (arom.) 814 (1,4-di-subst. arom.)cm^{-1}. ^{1}H NMR $\delta = 0\cdot89$, t ($J = 7$ Hz, 3 H); 1·23–1·96, m (30 H);1·59, d ($J = 7$ Hz, 3 H); 3·39, dt ($J = 9\cdot5/7$ Hz, 1 H); 3·47–3·54, m (2 H); 3·69, dt ($J = 9/ 7$ Hz, 1 H); 3·74, dt ($J = 9\cdot5/7$ Hz, 1 H); 3·84–3·91, m (1 H); 4·05, t ($J = 7$ Hz, 2 H); 4·21, q ($J = 7$ Hz, 1 H); 4·58, t (br) ($J = 4$ Hz, 1 H); 6·98/8·16, AA′BB′ ($J = 8\cdot5$ Hz, 4 H); 7·18/7·59, AA′BB′ ($J = 8\cdot5$ Hz, 4 H),; 7·27/7·60, AA′BB′ ($J = 8\cdot5$ Hz, 4 H). MS (180°C) $m/z = 461$ (0·4 per cent, M–C$_{10}$H$_{20}$OTHP), 445 (0·3 per cent, M–OC$_{10}$H$_{20}$OTHP), 277 (50 per cent, HOC$_{10}$H$_{20}$OC$_6$H$_4$CO), 186 (77 per cent, HOC$_6$H$_4$C$_6$H$_4$OH), 85 (100 per cent, DHP + 1).

(*S*)-(−)-4-(10-Hydroxydecyloxy)benzoic acid [4′-(2-hexyloxypropanoyloxybiphenyl-4-yl] ester **10**. The THP ether was cleaved using standard conditions. Quantity: 3·8 g (5·4 mmol) **8**, catalyst: hydrochloric acid. Yield: 3·3 g (99 per cent), crystalline solid. Phase sequence Cr 116 (S_X 109–110) S_A 128·8 N* 135·5 I (dichloromethane/ petroleum ether), $[\alpha]_D^{23} = -25\cdot5°$ (CHCl$_3$, $c = 1$); for spectroscopic data see [15].

(*S*)-(−)-4-(10-Acryloyloxydecyloxy)benzoic acid [4′-(2-hexyloxypropanoyloxybiphenyl-4-yl] ester **11**. At 60°C, 164 mg (1·8 mmol) of acryloyl chloride were added dropwise to a solution of 900 mg (1·45 mmol) **10** and 192 mg (1·9 mmol) triethylamine in 17 ml of dry tetrahy-drofuran. The reaction mixture was stirred at 60°C for 30 min and at room temperature for 2 h. Ether and water were added. The organic solution was separated, dried (MgSO$_4$) and evaporated. The product was separated by column chromatography (dichloromethane) were recrys-tallized from ether. Yield: 500 mg (51 per cent), crystalline solid. Phase sequence Cr 61·8 S_C^* 93·9 S 110·7 I, $[\alpha]_D^{23} = -25\cdot5°$ (CHCl$_3$, $c = 0\cdot8$). IR(KBr) $v = 2928/2854$ (C–H), 1773, 1730 (br, both AlkC=O), 1607/1494 (arom.), 810 (1,4-disubst. arom.)cm^{-1}. ^{1}H NMR $\delta = 0\cdot89$, t ($J = 7$ Hz, 3 H); 1·19–1·52, m (18 H); 1·59, d ($J = 7$ Hz, 3 H); 1·62–1·71, m (4 H); 1·87, quint ($J = 7$ Hz, 2 H); 3·50, dtr ($J = 9/7$ Hz, 1 H); 3·70, dt ($J = 9/7$ Hz, 1 H); 4·05, t ($J = 7$ Hz, 2 H); 4·15, t ($J = 7$ Hz, 2 H); 4·21 q ($J = 7$ Hz, 1 H); 5·87, dd ($J = 10\cdot5/1\cdot5$ Hz, 1 H); 6·13, dd ($J = 17\cdot5/10\cdot5$ Hz, 1 H); 6·41, dd ($J = 17\cdot5/1\cdot5$ Hz, 1 H); 6·97/8·16 AA′BB′, ($J = 8\cdot5$ Hz, 4 H); 7·18/7·59, AA′BB′ ($J = 8\cdot5$ Hz, 4 H); 7·27/7·60, AA′BB′ ($J = 8\cdot5$ Hz, 4 H). MS (180°C) $m/z = 672$ (2·3 per cent, M$^+$), 516 (5·7 per cent, M–COCH(CH$_2$)OC$_6$H$_{13}$), 444 (1·4 per cent, OC$_6$H$_4$CO$_2$C$_6$H$_4$O), 331 (100 per cent, CH$_2$CHCO$_2$ (CH$_2$)$_{10}$OC$_6$H$_5$CO$_2$); MS high resolution calculated 672·365, found 672·366.

Fluorescent dye compounds **14a–c** were prepared analogously to **11**. Typical quantities: 0·46 mmol **13**, 0·5 mmol triethylamine, and 0·5 mmol acryloyl chloride. 2,6-Dioxo-(4-methoxynaphtho) [c,d]-*N*-(10-acryloyloxy-

decyl)piperidine **14a**: Yield 92 per cent. Mp, 85·0°C (petroleum ether/dichloromethane). IR (CHCl₃) v = 3022/ 2931/2857 (C–H), 1710 (C=O), 1690/1653 (imide), 1594/1583/1515 (arom.) cm⁻¹. UV λ_{max} = 364 nm. Fluorescence λ_{max} = 428 nm. ¹H NMR δ = 1·24–1·46, m (12 H); 1·64, quint (J = 7 Hz, 2 H); 1·71, quint (J = 7 Hz, 2 H); 4·12, s (3 H); 4·13, t (J = 7 Hz, 2 H); 4·15, t (J = 7 Hz, 2 H); 5·81, dd (J = 10·5/1·5 Hz, 1 H); 6·11, dd (J = 17·5/ 10·5 Hz, 1 H); 6·39, dd (J = 17·5/1·5 Hz); 7·04/8·55, AB (J = 8·5 Hz, 2 H); 7·69/8·55/8·59,, ABC (J_{AB} = 8 Hz, J_{BC} = 1 Hz, J_{AC} = 7·5 Hz, 3 H). MS (150°C) m/z = 437 (64 per cent M⁺), 382 (6 per cent, M–CH₂CHCO), 366 (5 per cent, M–CH₂CHCO₂), 241 (59 per cent, M–CH₂CHCO₂(CH₂)₉), 227 (100 per cent, M–CH₂CHCO₂(CH₂)₁₀), 55 (31 per cent, CH₂CHCO); MS high resolution calculated 437·219, found 437·220.

2,6-Dioxo-(4-hexyloxynaphtho) [c,d]-*N*-(10-acryloyl-oxydecyl)piperidine **14b**: Yield 58 per cent. Mp 69·4°C (petroleum ether/dichloromethane). IR (CHCl₃) v = 3021/ 2933/2857 (C–H), 1716 (C=O), 1694/1654 (imide), 1593/1582/1514 (arom.), cm⁻¹. UV λ_{max} = 367 nm. Fluorescence λ_{max} = 432 nm. ¹H NMR δ = 0·93, t (J = 7 Hz, 3 H); 1·24–1·46, m (16 H); 1·51–1·61, m (2 H); 1·65, quint (J = 7 Hz, 2 H); 1·72, quint (J = 7 Hz, 2 H); 1·98, quint (J = 7 Hz, 2 H); 4·13, t (J = 7 Hz, 2 H); 4·15 t (J = 7 Hz, 2 H); 4·27, t (J = 7 Hz, 2 H); 5·81, dd (10·5/1·5 Hz, 1 H); 6·12, dd (J = 17/10·5 Hz, 1 H); 6·39 (J = 17/1·5 Hz, 1 H); 7·02/8·54, AB (8·5 Hz, 2 H); 7·70/8·58/8·60, ABC (J_{AB} = 8 Hz, J_{BC} = 1 Hz, J_{AC} = 7 Hz, 3 H). MS (270°C) m/z = 507 (100 per cent, M⁺), 452 (6 per cent, M–CH₂CHCO), 436 (5 per cent, M–CH₂CHCO₂), 310 (5 per cent, M–CH₂CHCO₂(CH₂)₉); MS high resolution calculated 507·2974, found 507·2985.

2,6-Dioxo-(4,5-dimethoxynaphtho) [c,d]-*N*-(10-acryl-oyloxydecyl)piperidine **14c**; Yield 45 per cent. Mp. 163–164°C (petroleum ether/dichloromethane/ether). IR (CHCl₃) v = 3020/2933/2857 (C–H), 1718 (C=O), 1688/ 1647 (imide), 1592/1580 (aroms.) cm⁻¹ UV λ_{max} = 376 and 395 nm. Fluorescence λ_{max} = 418 and 437 nm. ¹H NMR δ = 1·24–1·45, m (12 H); 1·64, quint (J = 7 Hz, 2 H); 1·71, quint (J = 7·5 Hz, 2 H); 4·03, s (6 H); 4·13, t (J = 7·5 Hz, 2 H); 4·14, t (J = 7 Hz, 2 H); 5·80, dd (J = 10·5/1·5 Hz, 1 H); 6·11, dd (J = 17/10·5 Hz, 1 H); 6·39, dd (J = 17/1·5 Hz, 1 H); 7·04/8·57, AB (J = 8·5 Hz, 4 H). MS (150°C) m/z = 467 (71 per cent, M⁺), 412 (10 per cent, M–CH₂CHCO), 396 (8 per cent, M–CH₂CHCO₂), 299 (4 per cent M–CH₂CHCO₂(CH₂)₇), 285 (9 per cent, M–CH₂CHCO₂(CH₂)₈), 271 (81 per cent, M–CH₂CHCO₂(CH₂)₉), 257 (100 per cent, M–CH₂CHCO₂(CH₂)₁₀), 55 (28 per cent, CH₂CHCO); MS high resolution calculated 467·230, found 467·231.

Polyacrylates: General procedure: 500 mg of the mono-

mer or the monomer mixture were dissolved in 4 ml of dry toluene. Nitrogen was passed through the solution for 15 min. Recrystallized AIBN (8 mg) was added and the solution was stirred under an atmosphere of nitrogen at 70°C for two days. The (co)polymers were precipitated in cold methanol. The crude products were purified by column chromatography (dichloromethane/ether, increasing polarity), dissolved in dichloromethane and once again precipitated in cold methanol. The purified polymers were dried under reduced pressure. The composition of the copolymers was determined by UV spectroscopy.

Poly-(*S*)-10-[4′-(2-hexyloxypropanoyloxy)biphenyl-4-yloxycarbonyl-4-phenoxy]decyl acrylate **15A** (homopolymer): Yield 23 per cent; for further information see figure 4.

Copolymer **15B**: Yield 19 per cent; dye content 5 ± 1% w/w (from UV measurements); for further information see figure 4.

Copolymer **15C**: Yield 35 per cent; dye content 4 ± 1% w/w (from UV measurements); for further information see figure 4.

Copolymer **15D**: Yield 43 per cent; dye content 5 ± 1% w/w (from UV measurements); for further information see figure 4.

References

[1] Scherowsky, G., 1995, *Ferroelectric Polymers*, edited by H. S. Nalwa (Marcel Dekker Inc.), and references cited therein.

[2] Coles, H. J., Gleeson, H. F., Scherowsky, G., and Schliwa, A., 1990, *Molec. Crystals liq. Crystals Lett.*, **7**, 117.

[3] Takahashi, K., Ishibashi, S., and Yamamoto, F., 1993, *Ferroelectrics*, **148**, 255.

[4] Yuasa, K., Uchida, S., Sekiya, T., Hashimoto, K., and Kawasaki, K., 1991, *Ferroelectrics*, **122**, 53.

[5] Ringsdorf, H., and Schmidt, H.-W., 1984, *Makromolek. Chem.*, **185**, 1327.

[6] Scherowsky, G., Beer, A., and Coles, H. J., 1991, *Liq. Crystals*, **10**, 809.

[7] Heilmeier, G. H., and Zanoni, L. A., 1968, *Appl. Phys. Lett.*, **13**, 91.

[8] Bahadur, B., 1991, *Molec. Crystals liq. Crystals*, **209**, 39.

[9] Coles, H. J., and Gleeson, H. F., 1988, *Molec. Crystals liq. Crystals Lett.*, **6**, 53.

[10] Coles, H. J., Gleeson, H. F., and Kang, J. S., 1989, *Liq. Crystals*, **5**, 1243.

[11] Coles, H. J., Lester, G. A., and Owen, H., 1993, *Liq. Crystals*, **14**, 1039.

[12] Schönberger, N., Schinzel, E., Martini, T., and Rösch, G., 1979, DE 29 44 867 A1.

[13] Beer, A., Scherowsky, G., Owen, H., and Coles, H. J., to be published.

[14] Neises, B., and Steglich, W., 1978, *Angew. Chem.*, **90**, 556.

[15] Beer, A., 1994, Dissertation, TU Berlin.