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A novel series of styrene-based liquid crystal monomers displaying either nematic or chiral nematic phases

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A new series of liquid crystalline styrene-based monomers is described. These monomers are prepared by the DCC-mediated esterification reaction between 4-[1-(4-vinylphenoxy)undecyloxy]benzoic acid and a range of phenols chosen due to their proven utility in the synthesis of liquid crystals. Most members of the series display thermally stable (enantiotropic) nematic phases, although a few give only monotropic nematic phases. By incorporating the (*S*)-2-methylbutyl side chain, monomers that exhibit the chiral nematic phase can be obtained. Predictably, monomers derived from phenols containing an additional ring as substituent (e.g. 4-cyano-4'-hydroxybiphenyl) display relatively high transition temperatures. In contrast, monomers derived from simple 4-*n*-alkylphenols possess a nematic phase, which is accessible at moderate temperatures. In addition, a eutectic mixture derived from these monomers has a melting point only just above room temperature, which is an advantage for the fabrication of robust films via the *in situ* photopolymerization process. Standard free radical polymerization of a number of these monomers provides side chain liquid crystal polymers, SCLCPs, with mesophases that are stable over a wide temperature range. For a homologous series of SCLCPs containing a terminal *n*-alkyl chain on the mesogenic group, an unexpected but distinct odd–even effect is observed.

1. Introduction

The *in situ* photopolymerization of acrylate-containing mesogens is an excellent method of freezing the partial order of a liquid crystal (LC) into the solid phase [1–4]. Typically, a mixture containing a monofunctional and a bifunctional LC monomer, together with a photoinitiator, is fabricated into a thin film and treated to give the desired LC phase and molecular orientation. Illumination by UV light initiates free-radical polymerization forming a robust and thermally stable network, within which the arrangement of the mesogenic units is retained. This technique is used for the production of oriented polymer structures with bespoke optical properties with applications as polarizers, waveguides, optical filters, and waveplates [5]; for example, coloured films can be derived from the selective reflection of light from a ‘frozen’ chiral nematic (cholesteric) phase [6, 7]. Of particular interest is the fabrication of wide band reflective polarizers using polymerizable cholesterics by means of the introduction of a pitch gradient. Although LC acrylate derivatives are highly successful monomers for photopolymerization, it is expected that other

reactive polymerizable groups would help to broaden the utility of the technique and solve a number of practical problems. For example, vinyl ether [8, 9] and epoxide [10] LC monomers can be polymerized using cationic photoinitiators that are compatible with the presence of oxygen. Despite their ability to undergo polymerization with radical, cationic or anionic initiators, the potential of styrene-based LC monomers is relatively unexplored, presumably due to perceived difficulties in synthesis and poor mesogenicity [11–14].

Recently, we described a series of styrene-containing mesogens based upon the 4-cyanobiphenyl mesogenic unit, see figure 1 [15]. Most members of this series display a thermally stable nematic phase at readily accessible temperatures, and photopolymerization can be carried out at room temperature using spin-coated films prepared from an appropriate mixture of these compounds. Prior to this study, the few examples of LC styrenes which had been described gave only a very

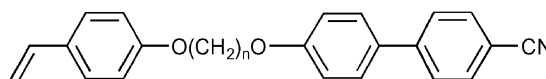
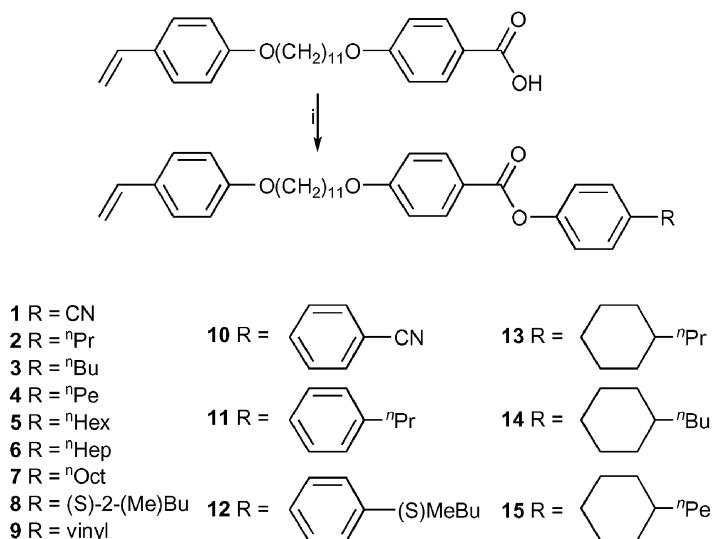


Figure 1. Structure of the cyanobiphenyl series of styrene-based LC monomers [14].

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Scheme 1. Synthesis of the LC styrene monomers **1–15**. Reagents and conditions: i, 4- $\text{RC}_6\text{H}_4\text{OH}$, DCC, 4-pyrrolidinopyridine, DCM, 25°C, 120 h.

narrow thermal range of nematic phase stability [12, 13] or a monotropic nematic phase (i.e. one which is observable only below the melting point of the compound during supercooling). One such example (**1**; scheme 1), described by Andersson and co-workers [11], was prepared by the ester-forming reaction between 4-cyanophenol and 4-[11-(4-vinylphenoxy)undecyloxy]benzoic acid (scheme 1). Despite the monotropic nature of the LC phase of **1**, it was anticipated that a similar synthetic procedure using a variety of other phenols, especially those commonly used in LC synthesis, could provide compounds that possess a nematic phase over a useful thermal range for *in situ* photopolymerizations.

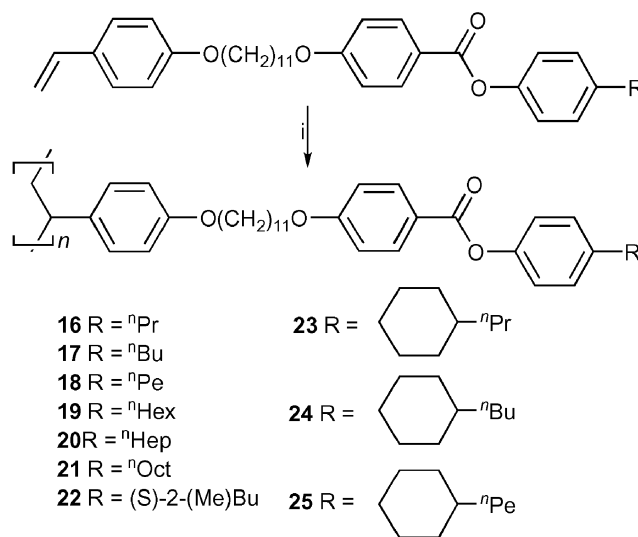
2. Results and discussion

2.1. Synthesis

Following a literature procedure [11], the important precursor, 4-[11-(4-vinylphenoxy)undecyloxy]benzoic acid, can be prepared in large quantities from commercially available 4-acetoxystyrene in four steps (overall yield=45%). The esterification of this benzoic acid derivative was achieved using the 1,3-dicyclohexylcarbodiimide (DCC) mediated reaction with a range of phenols chosen due to their proven utility in the synthesis of liquid crystals (scheme 1; table 1). The yield in these reactions varied from 15 to 70% with the solubility of the phenol in DCM appearing to be the limiting factor, particularly for the poor yields obtained for compounds **10–12**. The use of other solvents (e.g. THF) for the synthesis of these compounds was unsuccessful due to the stability of the *O*-acylisourea intermediate, which could be isolated in good yield

(~50%) from the reaction after several days [16]. The use of 1,2-dichloroethane as a higher boiling alternative to DCM gave undesired by-products as a result of the $\text{S}_{\text{N}}2$ reaction between solvent and phenolic anion.

As found in previous studies [11, 15], the resulting styrene monomers were indefinitely stable towards polymerization as solids without the need for stabilizers. However, free radical polymerization of monomers **1–8** and **13–15**, using AIBN in THF at 65°C, gave polymers **16–26** (scheme 2; Table 2). Attempted polymerization of monomers **10–12** under the same conditions gave solvent swollen gels and, due to the small quantities of



Scheme 2. Polymerization of the LC styrene monomers **1–8** and **13–15** to give polystyrenes **16–26**. Reagents and conditions: i, AIBN, THF, 65°C, 72 h.

Table 1. Yields and properties of monomers 1–15.

Monomer	Yield/%	$[\alpha]_{\text{D}}^{22}$ (CHCl ₃)	Crystal to nematic (K-N)/°C ($\Delta H/\text{kJ mol}^{-1}$)	Nematic to isotropic (N-I)/°C ($\Delta H/\text{kJ mol}^{-1}$)
1 ^a	62	—	93.3(58.2)	90.4(°)
2	40	—	65.9(46.8)	70.6(0.8)
3 ^a	50	—	64.3(54.2)	62.5(°)
4	42	—	66.6(46.4)	70.8(°)
5	59	—	59.3(63.1)	67.3(0.6)
6 ^b	35	—	58.9(41.8)	69.9(0.5)
7 ^b	41	—	52.5(67.7)	67.9(0.6)
8 ^{a, b}	65	+2.2	61.2(50.1)	46.8(°)
9	56	—	87.1(72.3)	94.2(1.3)
10	15	—	116.0(45.2)	214.0(0.8)
11	20	—	105.0(38.1)	168.2(0.9)
12 ^{c, d}	35	+2.1	96.1(52.1)	137.2(1.5)
13	40	—	96.8(50.2)	162.9(0.6)
14	38	—	82.8(43.4)	163.0(0.5)
15	36	—	95.3(49.7)	163.0(0.6)

^aMonomers 1, 3 and 8 exhibit a monotropic nematic phase. ^bMonomers 6 and 7 display a monotropic smectic A phase observable by microscopy only on rapid cooling. ^cMonomer 12 exhibits a monotropic blue phase on slow cooling above the isotropic to chiral nematic phase. ^dChiral nematic phase. ^eTransition not observed by DSC.

these monomers available for study, the appropriate conditions for polymerization of these three compounds was not determined. All monomers and polymers gave satisfactory elemental analyses and 1H NMR spectra consistent with their structures.

2.2. Thermal behaviour

Monomers 1–15 were examined using polarizing optical microscopy and differential scanning calorimetry (DSC), and the results are given in figure 2 and table 1. All of the non-chiral compounds exhibit the *schlieren* optical texture and a small enthalpy of transition from LC to isotropic liquid (0.5–3 kJ mol⁻¹) both of which are characteristic of the nematic phase. Monomers 1, 3 and 8 display only a monotropic phase. The monomers 5–7, derived from 4-*n*-alkyl phenols, possess the desired properties of an enantiotropic nematic phase together with a low melting point. The derivatives 6 and 7, which contain longer terminal alkyl chains, also display a

monotropic smectic A phase (onset ~25°C) that is only observable by rapid cooling of the compounds below their melting point. Branching in the terminal chain (e.g. (*S*)-2-methylbutyl) reduces the clearing temperature markedly, so that monomer 8 forms a monotropic chiral nematic phase (Grandjean optical texture) at a temperature which is some 20°C lower than the clearing temperature of the isomeric monomer 5. In contrast, monomer 9 possesses the highest clearing temperature of those compounds derived from a simple one-ring phenol, giving another example of the enhancement of the thermal stability of the nematic phase caused by a terminal vinyl group [15]. This difunctional monomer would be suitable as a network-forming component for *in situ* photopolymerization.

Mesogenic units containing a greater number of phenyl or cyclohexyl rings are known to provide greater thermal stability due to their enhanced rod-like shape. Therefore, it is unsurprising that monomers 10–15, which are derived from two-ring phenols, all display

Table 2. Yields and properties of polymers 16–25

Polymer (monomer)	Yield/%	$[\alpha]_{\text{D}}^{22}$ (CHCl ₃)	$M_{\text{n}} \times 10^{-3}$	$M_{\text{w}}/M_{\text{n}}$	Glass to smectic (g-Sm)/°C	Smectic to isotropic (Sm-I)/°C
16 (2)	47	—	13	1.8	42	112
17 (3)	35	—	14	1.5	62	89
18 (4)	50	—	57	1.9	50	117
19 (5)	57	—	46	2.0	49	104
20 (6)	63	—	48	1.8	38	110
21 (7)	63	—	59	1.9	45	103
22 (8)	52	+4.2	43	1.8	38	90
23 (13)	48	—	10	1.5	80	199
24 (14)	26	—	19	1.6	40	183
25 (15)	20	—	17	1.5	43	182

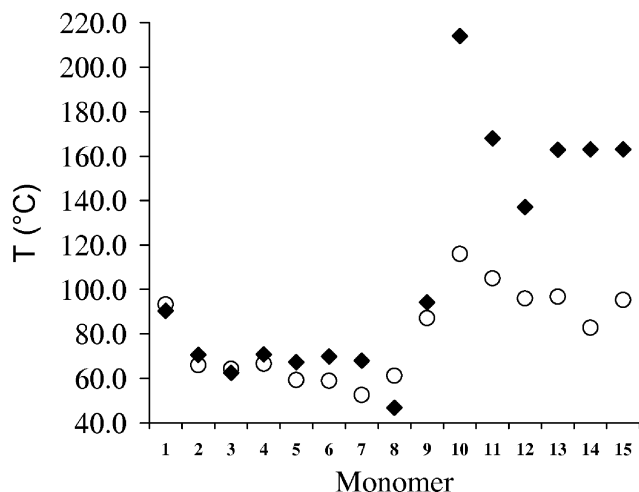


Figure 2. Diagrammatic representation of the thermal behaviour of monomers 1–15. For each compound \circ represents the crystal to nematic phase transition temperature and \blacklozenge represents the nematic (or chiral nematic for monomers 8 and 12) to isotropic (clearing) transition temperature. Compounds 1, 3 and 8 ($n=5$ and 10) show monotropic nematic phases. Monomers 6 and 7 display a monotropic smectic A phase observable by microscopy only on rapid cooling. Monomer 12 exhibits a monotropic blue phase on slow cooling above the isotropic to chiral nematic phase.

much higher clearing points. In particular, monomer 10 derived from 4-cyano-4'-hydroxybiphenyl has a clearing temperature which is 120°C higher than that of monomer 1, which is shorter by one phenyl ring. Similarly, monomers 11 and 12 have clearing temperatures which are $\sim 90^\circ\text{C}$ higher than those of the analogous monomers 4 and 8, respectively. Monomer 12 displays a monotropic blue phase (an example of a frustrated chiral phase) [17] on slow cooling of its isotropic phase to within $\sim 1^\circ\text{C}$ above the onset of the chiral nematic phase (Grandjean texture).

Photopolymerization is normally carried out at, or just above, room temperature. In LC technology it is usual for a mixture of compounds to be formulated in order to achieve desired properties such as a reduction in the crystal to liquid crystal transition temperature. It was found that a mixture containing 2 (25%), 4 (30%) and 6 (45%) displays a eutectic melting point of only 37°C with a clearing temperature of 69°C. On cooling, the nematic phase is retained at, or just above, room temperature (30°C) but further cooling gives a monotropic smectic A phase (onset = 25°C). These two phases can be maintained at readily accessible temperatures for an extended period before crystallization and, therefore, this mixture is particularly suitable for *in situ* photopolymerizations.

The polymers 16–22, and 23–25 prepared from solution free radical polymerization of the appropriate monomer, all display a liquid crystalline phase with the

classic 'sandy' texture, which is often encountered for side chain liquid crystals. As might be expected, the polymers containing three-ring mesogenic groups (23–25) display much higher transition temperatures than those containing two-ring mesogens (16–22). For all polymers, annealing over several hours gave a fine-grained texture, with homeotropic regions, consistent with the smectic A mesophase. This type of mesophase is commonly encountered for side chain liquid crystal polymers (SCLCPs) and is consistent with that found in previously described examples of polystyrene-based-SCLCPs prepared either from the polymerization of a styrene LC monomer [11–13, 15], as described here, or by grafting a mesogenic group onto preformed poly(4-hydroxystyrene) [18–22]. Non-smectogenic polystyrene-based liquid crystal polymers can be prepared by incorporation of a discotic mesogen which induces a hexagonal columnar mesophase [14] or by lateral attachment of a calamitic mesogen to the polymer backbone without a flexible spacer group to give a nematic LCP (so-called 'mesogen-jacketed' polymers) [23–26].

Polymers 16–21 contain mesogenic groups with terminal *n*-alkyl chains (propyl–octyl) and examination of the clearing temperatures of this homologous series (table 1 and figure 3) reveals a distinct odd–even effect; with the members of this series that contain an odd number of carbon atoms in the alkyl chain demonstrating significantly higher clearing transitions than those which possess an even number of carbon atoms. A similar, if much less pronounced, trend is observed for the corresponding monomers 2–7 (table 1, figure 2). Although odd–even effects have been observed for SCLCPs based on variation of the length of alkyl

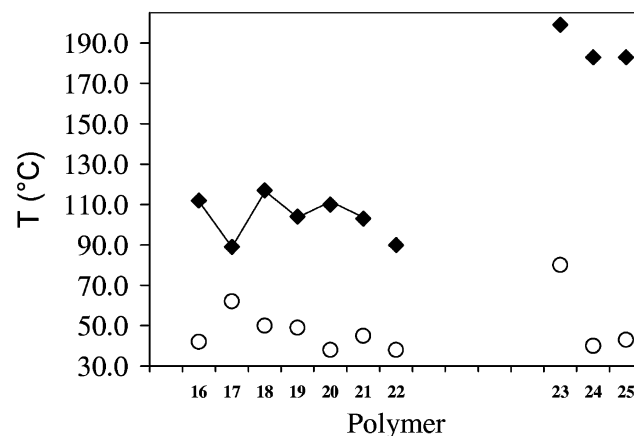


Figure 3. Diagrammatic representation of the thermal behaviour of polymers 16–22 and 23–25. For each polymer \circ represents the glass to smectic A transition phase and \blacklozenge represents the smectic A to isotropic (clearing) transition temperature. The odd–even effect for the clearing temperatures of the homologous series 16–21 (propyl–octyl) is illustrated.

spacer between the mesogen group and acrylate [27], methacrylate [28–30], siloxane [31], and indeed styrene [22] polymer backbones, the observation of such a distinct odd–even effect for a terminal alkyl chain is perhaps surprising.

To conclude, a number of novel liquid crystalline styrene-based monomers are described that possess thermally stable (enantiotropic) nematic or chiral nematic phases which form eutectic mixtures suitable for convenient film formation via *in situ* photopolymerization. Standard free radical polymerization of these monomers provides side chain liquid crystal polymers SCLCPs with mesophases that are stable over a wide temperature range. For a homologous series of these SCLCPs, which contain a terminal *n*-alkyl chain on the mesogenic group, an unexpected but distinct odd–even effect is observed.

3. Experimental

High resolution (500 MHz) ^1H NMR spectra were recorded using a Varian Unity 500 spectrometer. IR spectra were recorded on a ATI Mattson Genesis Series FTIR instrument (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low resolution chemical ionization (CI) mass spectra were obtained using a Fisons Instruments Trio 2000. Silica gel (60 Merck 9385) was used in the separation and purification of compounds by column chromatography. All materials were placed under vacuum for 18 h as the final step of purification. The intermediate, 4-[11-(4-vinylphenoxy)undecyloxy]benzoic acid, was made as described previously [11]. All phenol precursors were kindly supplied by Merck. Molecular mass was determined using gel permeation chromatography (GPC) using 3x PL Gel-Mixed B analytical columns (Polymer Laboratories) calibrated against polystyrene standards and using THF as eluant. Differential scanning calorimetry measurements were made on a Seiko DSC 220C machine and calibrated using an indium standard. Optical microscopy observations were made on a Nikon Optiphot-2 microscope with a Mettler FP80 HT hot stage.

3.1. 4-Cyanophenyl 4-[11-(4-vinylphenoxy)-undecyloxy]benzoate, 1

Following the method of Andersson *et al.* [11], a solution of 4-cyanophenol (3.89 g, 29 mmol), 4-[11-(4-vinylphenoxy)undecyloxy]benzoic acid (10.00 g, 24.4 mmol), 1,3-dicyclohexylcarbodiimide (6.04 g, 29.3 mmol) and 4-pyrrolidinopyridine (3.61 g, 24.4 mmol) in dry dichloromethane (200 ml) was stirred at 25°C for 120 h. The

resulting precipitate was removed by filtration and the solvent was removed under reduced pressure. The resulting solid was recrystallized from EtOH to give **1** as white crystals (7.75 g, 62%). Thermal transitions (°C): Cr 93.3 (N 90.4). Anal: found, C 77.45, H 7.35, N 2.82; $\text{C}_{33}\text{H}_{37}\text{NO}_4$ requires C 77.47, H 7.29, N, 2.74%. $\nu(\text{KBr})/\text{cm}^{-1}$, 2220 (CN), δ_{H} (CDCl_3 , 300 MHz, 25°C) 1.2–1.9 (18H, m), 3.99 (2H, t, *J* 7), 4.08 (2H, t, *J* 7), 5.17 (1H, d, *J* 11), 5.62 (1H, d, *J* 18), 6.69 (1H, dd, *J* 11,18), 6.89 (2H, d, *J* 9), 7.02 (2H, d, *J* 9), 7.19 (2H, d, *J* 9), 7.39 (2H, d, *J* 9), 7.79 (2H, d, *J* 9), 8.18 (2H, d, *J* 9). *m/z* (CI) 529 (M^+NH_4^+), 511 (M^+).

The monomers **2–15** were prepared using a similar procedure (see table 1).

3.2. Poly(4-propylphenyl 4[11-(4-vinylphenoxy)-undecyloxy]benzoate), 16

To a Pyrex glass ampoule was added **2** (0.3 g, 0.5 mmol), AIBN (0.6 mg, 3.1×10^{-3} mol), anhydrous THF (1.0 ml) and a magnetic stirrer bar. The mixture was cooled by liquid nitrogen and subjected to a high vacuum (~ 0.1 mm Hg). On warming, this degassing process was repeated twice further. The sealed ampoule was placed in an oil bath at 65°C and the solution stirred for 72 h. On cooling, the solution was added dropwise to petroleum ether (60/80) and the crude product collected by filtration. The polymer was purified by repeated precipitation from THF solution by adding to petroleum ether until no significant amount of monomer (i.e. less than 1%) was observed by ^1H NMR. The polymer was obtained as a white powder (141 mg, 47%): $M_n = 13 \times 10^3$ (average DP=25), $M_w/M_n = 1.8$. Thermal transitions (°C); g 42 Sm 112 I. Anal: found, C 79.5, H, 8.4%; $\text{C}_{35}\text{H}_{44}\text{O}_4$ requires C 79.51, H 8.39%. δ_{H} (CDCl_3 , 300 MHz, 25°C) 0.91 (3H, t, *J* 7), 1.1–1.9 (23H, br m), 2.62 (2H, t, *J* 8), 3.9–4.1 (4H, br m), 6.2–6.7 (4H, br m), 6.96 (2H, d, *J* 9), 7.11 (2H, d, *J* 9), 7.25 (2H, d, *J* 9), 8.17 (2H, d, *J* 9).

The polymers **17–25** were prepared using a similar procedure (see table 2).

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