JOURNAL OF Materials CHEMISTRY

Styrene-containing mesogens. Part 1: photopolymerisable nematic liquid crystals

Anthony Cook,[a] **Samer Badriya,**[a] **Simon Greenfield**[b] **and Neil B. McKeown***[a]

[a]*Department of Chemistry, University of Manchester, Manchester, UK M13 9PL. Tel: 0161 275 4710; Fax: 0161 275 4958; E-mail: neil.mckeown@man.ac.uk*
[b]*Merck Speciality Chemicals Ltd., NB-SC, UK, Chilworth Science Park, University Parkway, Chilworth, Southampton, Hampshire, UK SO16 7QD*

Received 23rd April 2002, Accepted 11th June 2002
First published as an Advance Article on the web 31st July 2002

Several members of a novel series of styrene-containing liquid crystal monomers, based on the cyanobiphenyl mesogenic group, possess thermally stable nematic phases. These materials display a large odd–even effect, relating to the length of the flexible spacer between the styrene and cyanobiphenyl units, which is very similar to previously described liquid crystal 'dimers' composed of two cyanobiphenyl units. It is shown that styrene (*i.e.* 4-vinylphenoxy) is an excellent terminal group for cyanobiphenyl mesogens as compared to a number of other phenyloxy groups. In addition, a compatible bifunctional mesogenic crosslinker is described. Photopolymerisation of an aligned film of a low-melting eutectic mixture derived from these compounds is achieved using cationic initiation in aerobic conditions.

Introduction

The *in-situ* photopolymerisation 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 polymerisation 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 films with bespoke optical properties; for example, the incorporation of dichroic dyes into the polymer network can produce polarising filters.[4] Similarly, coloured films can be derived from the selective reflection of light from a 'frozen' chiral nematic (cholesteric) phase.[3] Although LC acrylate derivatives are highly successful monomers for photopolymerisation,[5] it is expected that other reactive polymerisable groups would help to broaden the utility of the technique and solve a number of practical problems. Styrene derivatives, in common with vinyl ether[6,7] and epoxide[8] LC monomers, offer the possibility of polymerisation using cationic photoinitiators that would be compatible with the presence of oxygen. However, only a few examples of styrene-containing LC monomers have been described, to date. These display only a very narrow thermal range of LC phase stability or a monotropic phase (*i.e.* a LC phase that is observable only below the melting point of the compound during supercooling).[9–11] This paper introduces a series of styrene monomers **1** which contain cyanobiphenyl, one of the simplest and most ubiquitous of all mesogenic units. These materials displays only a nematic liquid crystal phase, relatively high clearing temperatures and a large odd–even effect (relating to the length of the flexible spacer between the styrene and cyanobiphenyl units). It is shown that the compatibility of styrene (4-vinylphenoxy) as a terminal group for cyanobiphenyl mesogens is excellent relative to a number of other phenyloxy groups. In addition, a compatible bifunctional LC styrene that allows the formulation of suitable mixtures for successful *in-situ* photopolymerisation is described.

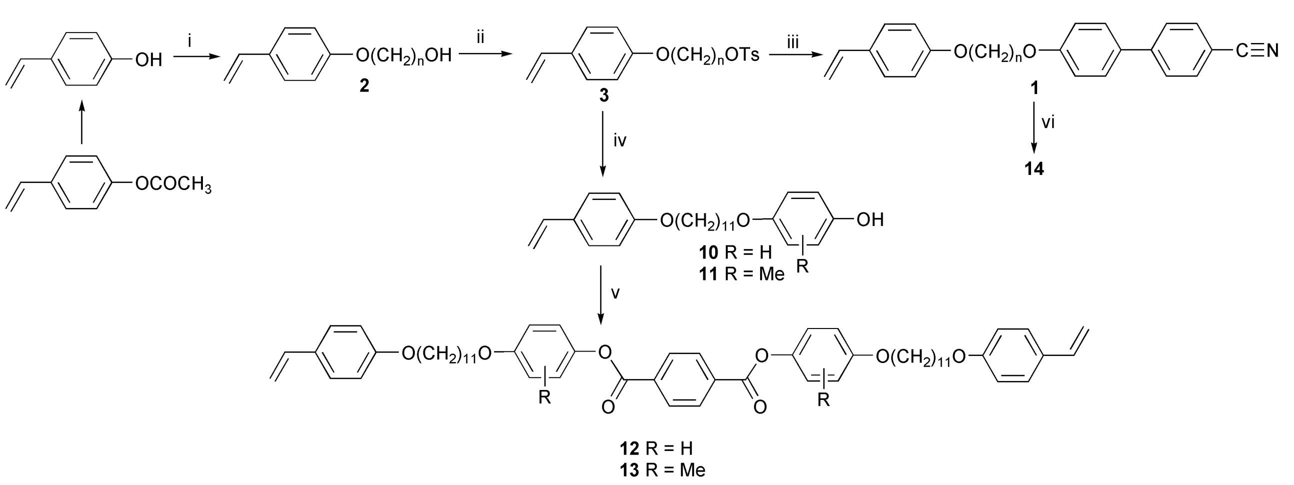
Results and discussions

Synthesis

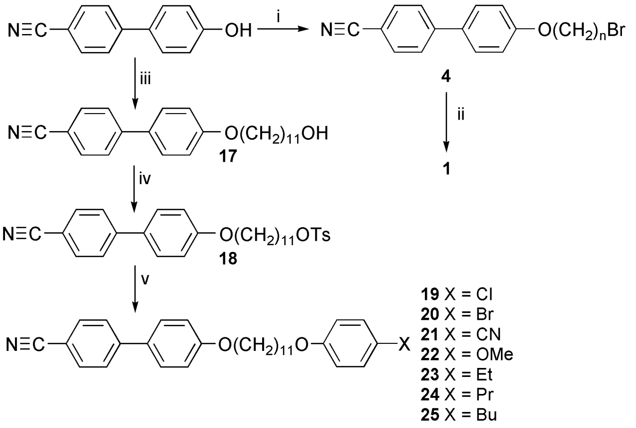
Two synthetic routes (Schemes 1 and 2) were found bo be convenient for the synthesis of series **1**. Hydrolysis of the commercially available 4-acetoxystyrene yields 4-hydroxystyrene that, despite its reputation for instability, can be stored indefinitely at −15 °C as a solution in diethyl ether. This compound reacts with the appropriate ω-bromo-α-hydroxyalkane to give the alcohol intermediate **2**. Tosylation of **2** gives **3** from which the styrenes **1** (n = 5–8, 11) were prepared by reaction with 4′-hydroxy-4-cyanobiphenyl as outlined in Scheme 1.[12] Alternatively, 4′-hydroxy-4-cyanobiphenyl was reacted with a suitable ω,α-dibromoalkane to give intermediate **4** from which **1** (n = 4, 9, 10) were prepared by reaction with 4-hydroxystyrene as shown in Scheme 2. Generally, both routes are equally suitable for the preparation of members of series **1** as they give comparable overall yields in the range 30–60%. However, only the route depicted in Scheme 2 is suitable for the preparation of **1** (n = 4) due to the non-availability of 4-bromobutanol and the tendency of 4-chlorobutanol to form THF rather than **2** (n = 4) under the basic reaction conditions encountered in Scheme 1. Both synthetic routes to series **1** exploit the stability of the styrene residue towards mildly basic reaction conditions. They proved to be of greater convenience than the more cautious strategy that uses a Wittig reaction to form the styrene unit in the final step of the scheme.[9] However, this latter method (Scheme 3), was used in initial work concerning the preparation of styrenes **5** (n = 6, 11) and **6** (n = 6, 11) *via* intermediates **7**, **8** and **9**. These styrene derivatives did not prove to be mesogenic. The bifunctional styrenes **12** and **13** are derived from tosylate **3** (n = 11), *via* **10** and **11**, respectively, as outlined in Scheme 1.

The styrene-containing compounds appear indefinitely stable towards polymerisation as solids and can be stored in ambient conditions without the need for stabilisers. However, polymerisation of **1** (n = 4–11), **5** and **6** to give polymers **14** (n = 4–11), **15** and **16**, respectively, was achieved readily by free radical initiation using AIBN in THF at 65 °C. Cyanobiphenyls **19–25** were prepared from 4-hydroxy-4′-cyanobiphenyl

DOI: 10.1039/b203940k

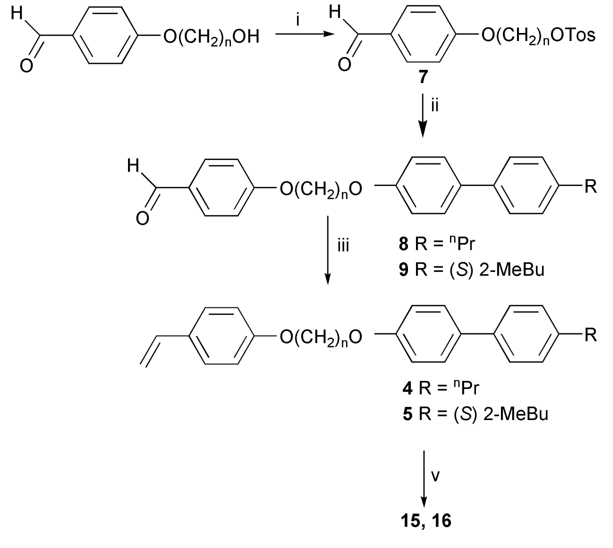


Scheme 1 *Reagents and conditions*: i, ω-bromo-α-hydroxyalkane, EtOH, NaOH, reflux; ii, TsCl, py, 0 °C; iii, 4′-hydroxy-4-cyanobiphenyl, anhydrous K_2CO_3, DMF, 80 °C; iv, hydroquinone, EtOH, NaOH, reflux; v, terephthaloyl chloride, py, dimethoxyethane, reflux; vi, AIBN, THF, 65 °C.



Scheme 2 *Reagents and conditions*: i, excess α,ω-dibromoalkane, anhydrous K_2CO_3, MEK, 80 °C; ii, 4-hydroxystyrene, anhydrous K_2CO_3, MEK, 80 °C; iii, ω-bromo-α-hydroxyalkane, EtOH, NaOH, reflux; iv, TsCl, py, 0 °C; v, 4-XC_6H_4OH, anhydrous K_2CO_3, MEK, 80 °C.

via intermediates **17** and **18** using ether forming reactions as outlined in Scheme 2. Spectroscopic analysis confirmed the structure of each compound and all mesogens provided a satisfactory elemental analysis.



Scheme 3 *Reagents and conditions*: i, TsCl, py, 0 °C; ii, v, 4-hydroxy-4′-alkylbiphenyl, anhydrous K_2CO_3, DMF, 80 °C; iii, methyltriphenylphosphonium bromide, *t*-BuOK, THF; iv, AIBN, THF, 65 °C.

Thermal behaviour

Series **1** was examined using polarising optical microscopy and differential thermal calorimetry (DSC) and the results are given in Fig. 1 and Table 1. All of the compounds exhibit the *Schlieren* optical texture and a small enthalpy of transition from LC to isotropic liquid (0.5–5 kJ M^{-1}) both of which are characteristic of the nematic phase. For **1** (n = 5 and 10) the nematic phase is monotropic. A comparison of the thermal

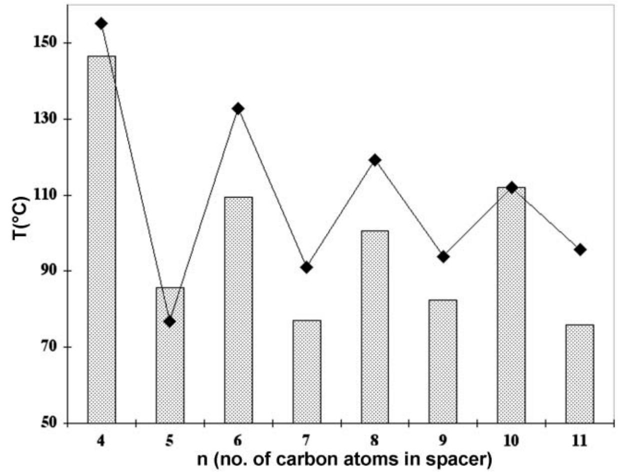


Fig. 1 A diagramatic representation of the thermal behaviour of series **1**. For each compound the shaded bar represents the crystal phase and ◆ represents the nematic to isotropic (clearing) transition temperature. Compounds **1** (n = 5 and 10) show monotropic nematic phases which are observable only on supercooling below the crystal to isotropic liquid transition.

Table 1 Temperature (ΔH/kJ mol^{-1}, ΔS/J K^{-1} mol^{-1}) of phase transitions of series **1** and bifunctional mesogens **12** and **13**

	Crystal to nematic (K–N)/°C	Nematic to isotropic (N–I)/°C
1 (n = 4)	146.5 (46.8, 111)	155.0 (2.1, 5)
1 (n = 5)[a]	85.6 (54.2, 150)	76.7 (0.7, 2)
1 (n = 6)	109.4 (46.4, 121)	132.7 (3.5, 8)
1 (n = 7)	77.0 (63.1, 180)	91.0 (1.1, 3)
1 (n = 8)	100.5 (41.8, 111)	119.1 (2.3, 6)
1 (n = 9)	82.5 (26.4, 74)	92.8 (0.4, 1)
1 (n = 10)[a]	112.1 (32.5, 83)	111.9 (3.5, 9)
1 (n = 11)	75.8 (67.7, 194)	95.7 (1.2, 3)
12	105.0 (74.2, 196)	145.1 (0.4, 1)
13	73.0 (71.7, 200)	108.3 (1.9, 5)

[a] Compounds **1** (n = 5 and 10) exhibit a monotropic nematic phase.

behaviour of series **1** with that of the much studied 4′-alkoxy-4-cyanobiphenyl homologous series[13] reveals that the terminal 4-vinylphenoxy (styrene) group results in both higher melting and clearing transition temperatures. It addition, the styrene group prevents formation of the smectic A mesophase which is prevalent in the 4′-alkoxy-4-cyanobiphenyl series for members with long alkyl chains (>heptyloxy). Another interesting feature of series **1** is the much higher transition temperatures for those compounds which possess an even number of atoms in the flexible linkage between the styrene and cyanobiphenyl units (n = 5, 7, 9, 11). The odd–even effect is associated with the lowest energy (*i.e.* all-*anti*) conformation of the alkyl spacer. Thus, a spacer containing an even number of atoms encourages the two rigid aromatic units to lie parallel to one another thereby enhancing the rod-like character of the molecule and raising the transition temperatures. An odd–even effect is also apparent for the entropy change associated with the nematic to isotropic transition. Members of series **1** containing a spacer with an even number of atoms (n = 4, 6, 8, 10) demonstrate a larger entropy change (5–9 J K^{-1} mol^{-1}) than that (1–3 J K^{-1} mol^{-1}) shown by compounds with an odd number of atoms in the spacer (n = 5, 7, 9, 11). These 'odd–even' effects and the absence of a smectic phase is highly reminiscent of the thermal behaviour of compounds which possess two mesogenic groups linked by a flexible spacer (termed LC 'dimers') such as the α,ω-bis(4′-cyano-4-biphenyloxy)-alkanes.[14,15]

The bifunctional styrenes **12** and **13** display the nematic phase over a large thermal range (>30 °C). The two lateral methyl substituents of **13** suppresses the transition temperatures by ~30 °C relative to **12** (Table 1). The benefit of small lateral substituents for lowering the transition temperatures of bifunctional cross-linking mesogens has been noted for similar acrylate derivatives.[16]

The synthesis of compounds **19–25** (Scheme 2) allowed a non-systematic assessment of the beneficial effect of the vinyl group found in series **1**. Compounds **19–25** have the same spacer as **1** (n = 11) but different substituents (X = Cl, Br, CN, OMe, Et, Pr, Bu) on the 4-position of the phenoxy group. A comparison of the thermal behaviour of **1** (n = 11) with those of **19–25**, shows that the vinyl group is the only terminal group compatible with a thermally stable (*i.e.* entiomeric) nematic phase (Fig. 2).

The polymers **14** (n = 6–11), **15** and **16**, all display a liquid crystalline phase with the classic 'sandy' texture which is often encountered for side-chain liquid crystals. Annealing over several hours gave a fine-grained texture, with homeotropic regions, consistent with Smectic A. Series **14** have been prepared previously by grafting the mesogenic side-chains onto poly(4-hydroxystyrene).[17] The transition temperatures obtained in both studies are similar, although the absence of liquid crystallinity for **14** (n = 4 and 5) is anomalous.

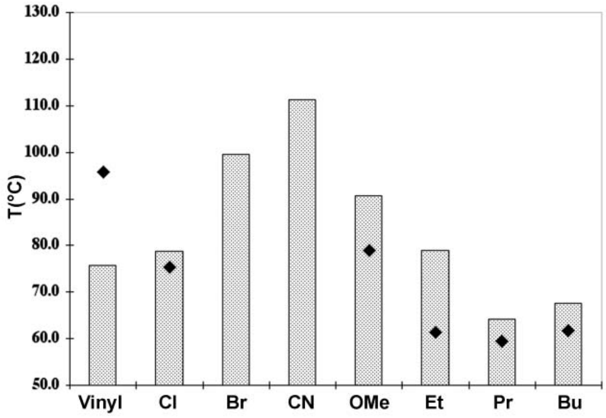


Fig. 2 A diagramatic comparison of the thermal behaviour of **1** (n = 11) and compounds **19–25**. For each compound the shaded bar represents the crystal phase and ◆ represents the nematic to isotropic (clearing) transition temperature. For X = Cl, OMe, Et, Pr and Bu only monotropic nematic phases are observable on supercooling below the crystal to isotropic liquid transition. For X = CN and Br no mesophase was observed on heating or cooling.

Photopolymerisation studies

Photopolymerisation 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 crystal to liquid crystal transition temperature. It was found that a mixture containing an equal amount of the lower melting members of series **1** (n = 5, 7, 11) displays a eutectic melting point of 42 °C with a clearing temperature of 88 °C. On cooling, the nematic phase is retained at room temperature for an extended period before crystallisation and, therefore, this mixture is particularly attractive for *in-situ* photopolymerisation. Bifunctional styrene **13** has a solid to nematic transition temperature below, and a clearing temperature above, that of the three components of the eutectic mixture. Thus, it was anticipated that this material would be a suitable cross-linking agent for network formation for this mixture. Indeed up to 30%, by mass, of **13** does not have a significant effect on the transition temperature of the eutectic mixture.

For the photopolymerisation experiments, films were deposited onto a glass substrate coated with rubbed polyimide by spin-coating a 10% (w/w) solution of the eutectic mixture containing cross-linker **13** in toluene–xylene–isopropyl alcohol (4 : 2 : 1) at 3000 rpm. These solutions also contained a cationic photoinitiator system composed of 1%, by mass, of diphenyliodonium hexaflourophosphate and a similar amount of phenothiazine photosensitiser. Photopolymerisation was achieved at 65 °C in air using a filtered UV light source (Blak-Ray B100 AP) with a narrow emission band at 360 nm. For films containing 30% (w/w) of cross-linker **13**, extraction of the resulting film with THF gave only residual (<1%) amounts of unreacted monomer. Films with 10% (w/w) cross-linker **13** gave up to 15% unreacted monomer. The resulting films were indistinguishable in appearance from the uncured oriented film using polarising microscopy and exhibited excellent mechanical resilience. Similar results were obtained using free radical photoinitiator (Irgacure 651) under a nitrogen atmosphere. This work demonstrates that cyanobiphenyl-based styrene monomers provide a versatile alternative to acrylate liquid crystals for *in-situ* photopolymerisation.

Experimental

High resolution (500 MHz) ^{1}H NMR spectra were recorded using a Varian Unity 500 spectrometer. IR spectra were recorded on a ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low-resolution chemical ionisation (CI) mass spectra were obtained using a Fisons Instruments Trio 2000. All solvents were dried and purified as described in ref. 18. 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 hours as the final step of purification. The intermediate, 11-(4′-cyanobiphenyloxy)-undecan-1-ol, (Scheme 3) was made by the reaction of 4-cyano-4′-hydroxybiphenyl, kindly supplied by Merck, with 11-bromoundecan-1-ol.[19,20] 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 eluent. 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.

4-(11-Hydroxyundecyloxy)styrene 2 (n = 11)

Following the method of Andersson *et al.*,[10] 4-acetoxystyrene (35.47 g, 218.9 mmol) was added to a stirred solution of KOH (35.47 g, 633 mmol) in EtOH (300 ml). After 1 h, sodium ethoxide (16.24 g, 238.8 mmol) was added and the mixture was heated to reflux for 0.5 h. A solution of 11-bromo-1-undecanol (54.24 g, 218.9 mmol) in EtOH (300 ml) was added and the solution was heated at reflux for 20 h. Removal of the solvent under reduced pressure gave a viscous oil to which was added aq. $NaHCO_3$ (10% w/w, 600 ml). The product was extracted using CH_2Cl_2 (3 × 100 ml), washed with aq. NaOH (1.0 M, 2 × 400 ml) and water (600 ml). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was recrystallised from hexane to give **2** (n = 11) as white crystals (56.45 g, 78%): mp 73 °C (Found: C, 78.05; H, 10.4%. $C_{19}H_{30}O_2$ requires C, 78.55; H, 10.4%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–1.9 (18H, m), 3.63 (2H, t, *J* 7), 4.00 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.78 (1H, dd, *J* 11,18), 6.88 (2H, d, *J* 9), 7.38 (2H, d, *J* 9); *m*/*z* (CI) 308 ($M^+ + NH_4^+$), 268 (M^+).

The following compounds were prepared using a similar procedure.

4-(5-Hydroxypentyloxy)styrene 2 (n = 5)

The crude product (12.24 g, 71%) was obtained as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.5–1.9 (6H, m), 3.70 (2H, t, *J* 7), 4.00 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.70 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.38 (2H, d, *J* 9); *m*/*z* (CI) 224 ($M^+ + NH_4^+$), 206 (M^+).

4-(6-Hydroxyhexyloxy)styrene 2 (n = 6)

The crude product (7.52 g, 65%) was obtained as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.3–1.9 (8H, m), 3.70 (2H, t, *J* 7), 4.00 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.63 (1H, dd, *J* 11,18), 6.87 (2H, d, *J* 9), 7.39 (2H, d, *J* 9); *m*/*z* (CI) 238 ($M^+ + NH_4^+$), 220 (M^+).

4-(7-Hydroxyheptyloxy)styrene 2 (n = 7)

The product (4.30 g, 71%) was obtained as a viscous colourless oil (Found: C, 77.20; H, 9.50%. $C_{15}H_{22}O_2$ requires C, 76.90; H, 9.45%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.3–1.9 (10H, m), 3.68 (2H, t, *J* 7), 4.00 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.71 (1H, dd, *J* 11,18), 6.87 (2H, d, *J* 9), 7.39 (2H, d, *J* 9); *m*/*z* (CI) 252 ($M^+ + NH_4^+$), 235 (M^+).

4-(8-Hydroxyoctyloxy)styrene 2 (n = 8)

The crude product (10.70 g, 72%) was obtained as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.3–1.9 (12H, m), 3.65 (2H, t, *J* 7), 4.00 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.70 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.38 (2H, d, *J* 9); *m*/*z* (CI) 266 ($M^+ + NH_4^+$), 249 (M^+).

4-[11-(*p*-Tosyloxy)undecyloxy]styrene 3 (n = 11)

A solution of **2** (n = 11) (47.24 g, 176 mmol) in CH_2Cl_2 (300 ml) was added dropwise to a stirred solution of *p*-tosyl chloride (39 g, 205 mmol) in pyridine (150 ml) and CH_2Cl_2 (500 ml). Stirring was continued for 6 h after which TLC analysis indicated the absence of the alcohol. The mixture was washed with aq. HCl (1 M, 3 × 500 ml), aq. NaOH (2 M, 2 × 400 ml) and water (400 ml). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was purified by column chromatography (eluent: toluene) to give **3** as a viscous colourless oil (63.42 g, 81%) (Found: C, 69.88; H, 8.47; S, 7.25%. $C_{26}H_{36}O_4S$ requires C, 70.25; H, 8.15; S, 70.25%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–1.5 (14H, m), 1.68–1.73 (4H, m), 2.44 (3H, s), 3.95–4.00 (4H, m), 5.14 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.35 (2H, d, *J* 9), 7.65 (2H, d, *J* 9), 7.83 (2H, d, *J* 9); *m*/*z* (CI) 462 ($M^+ + NH_4^+$), 445 (M^+).

The following compounds were prepared using a similar procedure.

4-[5-(*p*-Tosyloxy)pentyloxy]styrene 3 (n = 5)

The crude product (10.03 g, 55%) was obtained from **2** (n = 5) as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–2.0 (6H, m), 2.44 (3H, s), 3.95–4.00 (4H, m), 5.14 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.35 (2H, d, *J* 9), 7.65 (2H, d, *J* 9), 7.83 (2H, d, *J* 9); *m*/*z* (CI) 378 ($M^+ + NH_4^+$), 361 (M^+).

4-[6-(*p*-Tosyloxy)hexyloxy]styrene 3 (n = 6)

The crude product (6.35 g, 60%) was obtained from **2** (n = 6) as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.36–1.43 (4H, m), 1.68–1.73 (4H, m), 2.44 (3H, s), 3.93 (2H, t, *J* 7), 4.08 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.25 (2H, d, *J* 9), 7.65 (2H, d, *J* 9), 7.83 (2H, d, *J* 9); *m*/*z* (CI) 392 ($M^+ + NH_4^+$), 375 (M^+).

4-[7-(*p*-Tosyloxy)heptyloxy]styrene 3 (n = 7)

The product (6.93 g, 89%) was obtained from **2** (n = 7) as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.36–1.43 (6H, m), 1.68–1.73 (4H, m), 2.48 (3H, s), 3.96 (2H, t, *J* 7), 4.08 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.85 (2H, d, *J* 9), 7.25 (2H, d, *J* 9), 7.65 (2H, d, *J* 9), 7.83 (2H, d, *J* 9); *m*/*z* (CI) 392 ($M^+ + NH_4^+$), 375 (M^+).

4-[8-(*p*-Tosyloxy)octyloxy]styrene 3 (n = 8)

The product (6.93 g, 89%) was obtained from **2** (n = 8) as a viscous colourless oil which was used without further purification: δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.15–1.90 (12H, m), 2.44 (3H, s), 3.98 (2H, t, *J* 7), 4.18 (2H, t, *J* 7), 5.18 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.88 (2H, d, *J* 9), 7.25 (2H, d, *J* 9), 7.40 (2H, d, *J* 9), 7.83 (2H, d, *J* 9); *m*/*z* (CI) 392 ($M^+ + NH_4^+$), 375 (M^+).

4-(6-*p*-Tosyloxy)hexyloxybenzaldehyde 7 (n = 6)

The product (14.28 g, 59%) was obtained from 6-(4-formylphenoxy)hexan-1-ol as colourless crystals: mp 76 °C (MeOH) (Found: C, 63.85; H, 6.6; S, 8.8%. $C_{20}H_{24}O_5S$ requires C, 63.8; H, 6.45; S, 8.5%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.20–1.90 (8H, m), 2.44 (3H, s), 3.98–4.08 (4H, m), 6.94 (2H, d, *J* 9), 7.35 (2H, d, *J* 9), 7.81 (4H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 394 ($M^+ + NH_4^+$).

4-(11-*p*-Tosyloxy)undecyloxybenzaldehyde 7 (n = 11)

The product (12.56 g, 57%) was obtained from 6-(4-formylphenoxy)undecan-1-ol as colourless crystals: mp 52 °C (hexane) (Found: C, 67.1; H, 7.75; S, 7.1%. $C_{25}H_{34}O_5S$ requires C, 67.25; H, 7.65; S, 7.2%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.10–1.90 (18H, m), 2.44 (3H, s), 3.98–4.08 (4H, m), 6.98 (2H, d, *J* 9), 7.35 (2H, d, *J* 9), 7.81 (4H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 464 ($M^+ + NH_4^+$), 447 (M^+).

4-(11-*p*-Tosyloxy)undecyloxy-4′-cyanobiphenyl 18

The product (7.9 g, 65%) was obtained from **17** as colourless crystals: mp 94 °C (EtOH) (Found: C, 71.68; H, 7.05; N, 2.59; S, 5.76%. $C_{31}H_{37}NO_4S$ requires C, 71.65; H, 7.18; N, 2.70; S, 6.17%); *ν*(thin film)/cm^{-1} 2224 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.10–1.90 (18H, m), 2.46 (3H, s), 3.98–4.08 (4H, m), 7.01 (2H, d, *J* 9), 7.36 (2H, d, *J* 9), 7.55 (2H, d, *J* 9), 7.66 (2H, d, *J* 9), 7.72 (2H, d, *J* 9), 7.81 (2H, d, *J* 9); *m*/*z* (CI) 537 ($M^+ + NH_4^+$), 519 (M^+).

4-(4-Bromobutyloxy)-4′-cyanobiphenyl 4 (*n* = 4)

To a solution of 4-hydroxy-4′-cyanobiphenyl (5.00 g, 25.6 mmol) and 1,4-dibromobutane (55.4 g, 256.4 mmol) in DMF (50 ml) was added K_2CO_3 (7.09 g, 51.3 mmol). The reaction was heated at 80 °C at 0.5 h. On cooling, the DMF and excess 1,4-dibromobutane were removed under reduced pressure. Water (50 ml) was added to the solid residue and the product was extracted with CH_2Cl_2, dried ($MgSO_4$) and evaporated to dryness under reduced pressure. The product was recrystallised from EtOH to give colourless crystals (6.90 g, 81%): thermal transitions (°C): K 57 N 65 I (Found: C, 62,25; H, 4.95; N, 4.23; Br, 23.6%. $C_{17}H_{16}BrNO$ requires C, 62.0; H, 4.92; N, 4.25; Br, 24.0%); *ν*(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 2.06–2.10 (4H, m), 3.55 (2H, t, *J* 7), 4.09 (2H, t, *J* 7), 7.02 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.72 (2H, d, *J* 9); *m*/*z* (CI) 349 ($M^+ + NH_4^+ + 2$), 347 ($M^+ + NH_4^+$), 331 ($M^+ + 2$), 329 (M^+).

The following compounds were prepared using a similar procedure.

4-(9-Bromononyloxy)-4′-cyanobiphenyl 4 (*n* = 9)

The product was obtained using 1,9-dibromononane and recrystallised from EtOH to give colourless crystals (3.06 g, 87.8%): thermal transitions (°C); K 68.3 (N 65.0) I (Found: C, 65.98; H, 6.67; N, 3.55; Br, 20.22%. $C_{22}H_{26}BrNO$ requires C, 66.27; H, 6.52; N, 3.51; Br, 20.05%); *ν*(thin film)/cm^{-1} 2222 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.33–1.53 (10H, br m), 1.88 (4H, m), 3.45 (2H, t, *J* 7), 4.05 (2H, t, *J* 7), 7.03 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.68 (2H, d, *J* 9), 7.74 (2H, d, *J* 9); *m*/*z* (CI) 419 ($M^+ + NH_4^+ + 2$), 417 ($M^+ + NH_2^+$), 401 ($M^+ + 2$), 399 (M^+).

4-(10-Bromodecyloxy)-4′-cyanobiphenyl 4 (*n* = 10)

The product was obtained using 1,10-dibromodecane and recrystallised from EtOH to give colourless crystals (2.57 g, 87.9%): thermal transitions (°C): K 63.3 (N 64.9) I (Found: 66.80; H, 6.76; N, 3.34; Br, 19.41%. $C_{23}H_{28}BrNO$ requires C, 66.67; H, 6.81; N, 3.38; Br, 19.28%); *ν*(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.30–1.56 (12H, br m), 1.88 (4H, m), 3.45 (2H, t, *J* 7), 4.02 (2H, t, *J* 7), 7.0 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.56 (2H, d, *J* 9), 7.70 (2H, d, *J* 9); *m*/*z* (CI) 433 ($M^+ + NH_4^+ + 2$), 431 ($M^+ + NH_4^+$), 415 ($M^+ + 2$), 413 (M^+).

4-(11-Hydroxyundecyloxy)-4′-cyanobiphenyl 17

The product was obtained using 11-bromoundecan-1-ol and recrystallised from EtOH to give colourless crystals (9.07 g, 82%): thermal transitions (°C): K 89.8 N 92.0 I (Found: 79.16; H, 9.00; N, 3.86%. $C_{24}H_{31}NO_2$ requires C, 78.89; H, 8.55; N, 3.83%); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.20–1.62 (16H, br m), 1.78–1.85 (4H, m), 3.66 (2H, t, *J* 6), 4.02 (2H, t, *J* 6), 7.02 (2H, d, *J* 9), 7.55 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m*/*z* (CI) 383 ($M^+ + NH_4^+$), 365 (M^+).

4-[4-(4-Vinylphenyloxy)butyloxy]-4′-cyanobiphenyl 1 (*n* = 4)

To a solution of KOH (1 g, 18 mmol) in EtOH (8 ml) was added 4-acetoxystyrene (0.8 g, 5.4 mmol). After 1 h, sodium ethoxide (0.4 g, 5.8 mmol) was added and the mixture was heated to reflux for 0.5 h. A solution of **4** (*n* = 4) (1.8 g, 5.4 mmol) in EtOH (8 ml) was added and the solution was heated at reflux for 20 h. Removal of the solvent under reduced pressure gave a solid residue which was dissolved in CH_2Cl_2 (50 ml), washed with aq. NaOH (1.0 M, 2 × 10 ml) and water (20 ml). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was recrystallised from CH_2Cl_2–EtOH to give **1** (*n* = 4) as white crystals (1.52 g, 76%): thermal transitions (°C): K 146.5 N 155.0 I (Found: C, 81.23; H, 6.15; N, 3.70%. $C_{25}H_{23}NO_2$ requires C, 81.25; H, 6.30; N, 3.80%); *ν*(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.9–2.1 (4H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 387 ($M^+ + NH_4^+$), 369 (M^+).

The following compounds were prepared using a similar procedure.

4-[9-(4-Vinylphenyloxy)nonyloxy]-4′-cyanobiphenyl 1 (*n* = 9)

The crude product was obtained from **4** (*n* = 9) and recrystallised from EtOH to give white crystals (1.03 g, 38%): thermal transitions (°C): K 82.5 N 92.8 I (Found: C, 82.01; H, 7.74; N, 3.14%. $C_{30}H_{33}NO_2$ requires C, 81.97; H, 7.57; N, 3.19%); *ν*(KBr)/cm^{-1} 2225 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.37–1.57 (10H, m), 1.78–1.85 (4H, m), 4.0–4.0 (4H, m), 5.16 (1H, d, *J* 11), 5.64 (1H, d, *J* 18), 6.70 (1H, dd, *J* 11,18), 6.89 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.36 (2H, d, *J* 9), 7.56 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m*/*z* (CI) 457 ($M^+ + NH_4^+$), 439 (M^+).

4-[10-(4-Vinylphenyloxy)decyloxy]-4′-cyanobiphenyl 1 (*n* = 10)

The crude product was obtained from **4** (*n* = 10) recrystallised from EtOH to give white crystals (0.86 g, 34%): thermal transitions (°C): K 112.1 (N 111.9) I (Found: C, 82.28; H, 7.96; N, 3.07%. $C_{31}H_{35}NO_2$ requires C, 82.08; H, 7.78; N, 3.09%); *ν*(KBr)/cm^{-1} 2226 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.37–1.57 (12H, m), 1.78–1.89 (4H, m), 4.0–4.1 (4H, m), 5.15 (1H, d, *J* 11), 5.64 (1H, d, *J* 18), 6.70 (1H, dd, *J* 11,18), 6.89 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.37 (2H, d, *J* 9), 7.56 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m*/*z* (CI) 471 ($M^+ + NH_4^+$), 453 (M^+).

4-[5-(4-Vinylphenyloxy)pentyloxy]-4′-cyanobiphenyl 1 (*n* = 5)

To a solution of 4-hydroxy-4′-cyanobiphenyl (1.7 g, 8.7 mmol) and **3** (*n* = 5) (2.76 g, 7.7 mmol) in DMF (50 ml) was added K_2CO_3 (2.8 g, 20 mmol). The reaction was heated at 80 °C for 0.5 h. On cooling, the DMF was removed under reduced pressure. Water (50 ml) was added to the solid residue and the product was extracted with CH_2Cl_2 (2 × 50 ml), dried ($MgSO_4$) and evaporated to dryness under reduced pressure. The product was purified by column chromatography (eluent: toluene) and recrystallisation from EtOH to give colourless crystals (2.21 g, 76%): thermal transitions (°C): K 85.6 (N 76.7) I (Found: C, 81.62; H, 6.70; N, 3.70%. $C_{26}H_{25}O_2N$ requires C, 81.40; H, 6.60; N, 3.65%); *ν*(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.7–2.1 (6H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 401 ($M^+ + NH_4^+$), 383 (M^+).

The following compounds were prepared using a similar procedure.

4-[6-(4-Vinylphenyloxy)hexyloxy]-4′-cyanobiphenyl 1 (*n* = 6)

The product was obtained from **3** (*n* = 6) and purified by column chromatography (eluent: toluene) and recrystallisation from EtOH to give colourless crystals (2.82 g, 68%): thermal transitions (°C): K 109.4 N 132.7 I (Found: C, 81.65; H, 6.75;

N, 3.50%. $C_{27}H_{27}NO_2$ requires C, 81.55; H, 6.85; N, 3.55%); ν(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.6–2.1 (8H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 417 (M$^+$ + NH$_4^+$), 398 (M$^+$).

4-[7-(4-Vinylphenyloxy)heptyloxy]-4′-cyanobiphenyl 1 (*n* = 7)

The product was obtained from **3** (*n* = 7) and purified by column chromatography (eluent: toluene) and recrystallisation from EtOH to give colourless crystals (5.54 g, 75%): thermal transitions (°C): K 77.0 N 91.0 I (Found: C, 81.2; H, 6.95; N, 3.25%. $C_{28}H_{29}NO_2$ requires C, 81.70; H, 7.1; N, 3.40%); ν(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.4–2.1 (10H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 429 (M$^+$ + NH$_4^+$), 412 (M$^+$).

4-[8-(4-Vinylphenyloxy)octyloxy]-4′-cyanobiphenyl 1 (*n* = 8)

The product was obtained from **3** (*n* = 8) and purified by column chromatography (eluent: toluene) and recrystallisation from EtOH to give colourless crystals (1.64 g, 48%): thermal transitions (°C): K 100.5 N 119.1 I (Found: C, 81.8; H, 7.45; N, 3.40%. $C_{29}H_{31}O_2N$ requires C, 81.85; H, 7.35; N, 3.3%); ν(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.3–2.1 (12H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 443 (M$^+$ + NH$_4^+$), 426 (M$^+$).

4-[11-(4-Vinylphenyloxy)undecyloxy]-4′-cyanobiphenyl 1 (*n* = 11)

The product was obtained from **3** (*n* = 11) and purified by column chromatography (eluent: toluene) and recrystallisation from EtOH to give colourless crystals (3.35 g, 77%): thermal transitions (°C): K 75.8 N 95.7 I (Found: C, 82.3; H, 8.15; N, 3.2%. $C_{32}H_{37}NO_2$ requires C, 82.2; H, 8.0; N, 3.0%); ν(KBr)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.1–2.1 (18H, m), 4.0–4.2 (4H, m), 5.04 (1H, d, *J* 11), 5.53 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.78 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.26 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.63 (2H, d, *J* 9); *m*/*z* (CI) 485 (M$^+$ + NH$_4^+$), 468 (M$^+$).

4-[11-(4-Vinylphenyloxy)undecyloxy]phenol 10

The product was derived from **3** (*n* = 11) and hydroquinone and purified by recrystallisation from hexane to give colourless crystals (4.56 g, 44%): mp 83 °C (Found: C, 75.5; H, 9.0%. $C_{25}H_{34}O_3$ requires C, 78.5; H, 8.95%); ν(KBr)/cm^{-1} 3365 (OH); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.1–2.0 (18H, m), 4.0–4.2 (4H, m), 4.57 (1H, br s), 5.17 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.68 (1H, dd, *J* 11,18), 6.81 (2H, d, *J* 9), 6.89 (2H, d, *J* 9), 6.93 (2H, d, *J* 9), 7.39 (2H, d, *J* 9); *m*/*z* (CI) 400 (M$^+$ + NH$_4^+$), 383 (M$^+$).

2(3)-Methyl-4-[11-(4-vinylphenyloxy)undecyloxy]phenol 11

The product was obtained from **3** (*n* = 11) and 2-methylhydroquinone as a mixture of two isomers and purified by recrystallisation from hexane to give colourless crystals (8.74 g, 82%): mp 60–68 °C (Found: C, 78.75; H, 9.05%. $C_{26}H_{36}O_3$ requires C, 78.75; H, 9.15%); ν(KBr)/cm^{-1} 3365 (OH); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.1–2.0 (18H, m), 2.25 and 2.22 (3H, s), 4.0–4.2 (4H, m), 4.79 and 4.63 (1H, br s), 5.17 (1H, d, *J* 11), 5.63 (1H, d, *J* 18), 6.69 (3H, m), 6.89 (2H, d, *J* 9), 7.15 (1H, m), 7.39 (2H, d, *J* 9); *m*/*z* (CI) 414 (M$^+$ + NH$_4^+$), 397 (M$^+$).

4-[11-(4-Formylphenyloxy)hexyloxy]-4′-*n*-propylbiphenyl 8 (*n* = 6)

The product was obtained from **7** (*n* = 6) and 4-hydroxy-4′-*n*-propylbiphenyl and was used in the next step without further purification (5.42 g, 81%): δ_H (CDCl$_3$, 300 MHz, 25 °C) 0.93 (3H, t, *J* 7), 1.4–2.1 (10H, m), 2.62 (2H, t, *J* 7), 4.0–4.2 (4H, m), 6.93 (4H, m), 7.21 (2H, d, *J* 9), 7.48 (4H, m), 7.8 (2H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 434 (M$^+$ + NH$_4^+$), 417 (M$^+$).

4-[11-(4-Formylphenyloxy)undecyloxy]-4′-*n*-propylbiphenyl 8 (*n* = 11)

The product was obtained from **7** (*n* = 11) and 4-hydroxy-4’-*n*-propylbiphenyl and was used in the next step without further purification (6.31 g, 84%): δ_H (CDCl$_3$, 300 MHz, 25 °C) 0.93 (3H, t, *J* 7), 1.1–2.1 (20H, m), 2.62 (2H, t, *J* 7), 4.0–4.2 (4H, m), 6.93 (4H, m), 7.21 (2H, d, *J* 9), 7.48 (4H, m), 7.8 (2H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 504 (M$^+$ + NH$_4^+$), 487 (M$^+$).

4-[6-(4-Formylphenyloxy)hexyloxy]-4’-((*S*)-(+)-2-methylbutyl)-biphenyl 9 (*n* = 6)

The product was obtained from **7** (*n* = 6) and (*S*)-(+)-4-hydroxy-4′-(2-methylbutyl)biphenyl and was purified by recrystallisation from EtOH to give colourless crystals (1.93 g, 85%): mp 89 °C (Found: C, 81.05; H, 8.45%. $C_{30}H_{36}O_3$ requires C, 81.05; H, 8.5); δ_H (CDCl$_3$, 300 MHz, 25 °C) 0.90–0.93 (6H, m), 1.1–2.09 (11H, m), 2.39 (1H, q, *J* 7), 2.67 (1H, q, *J* 7), 4.0–4.2 (4H, m), 6.96 (4H, m), 7.16 (2H, d, *J* 9), 7.48 (4H, m), 7.81 (2H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 462 (M$^+$ + NH$_4^+$), 445 (M$^+$).

4-[11-(4-Formylphenyloxy)undecyloxy]-4′-((*S*)-(+)-2-methylbutyl)-biphenyl 9 (*n* = 11)

The product was obtained from **7** (*n* = 11) and (*S*)-(+)-4-hydroxy-4′-(2-methylbutyl)biphenyl and was purified by recrystallisation from EtOH to give colourless crystals (1.86 g, 83%): mp 53 °C (Found: C, 80.95; H, 8.95%. $C_{35}H_{46}O_3$ requires C, 81.65; H, 9.0); δ_H (CDCl$_3$, 300 MHz, 25 °C) 0.90–0.93 (6H, m), 1.1–2.09 (21H, m), 2.39 (1H, q, *J* 7), 2.67 (1H, q, *J* 7), 4.0–4.2 (4H, m), 6.96 (4H, m), 7.16 (2H, d, *J* 9), 7.48 (4H, m), 7.84 (2H, d, *J* 9), 9.89 (1H, s); *m*/*z* (CI) 532 (M$^+$ + NH$_4^+$), 515 (M$^+$).

4-[11-(4-Chlorophenyloxy)undecyloxy]-4′-cyanobiphenyl 19

The product was obtained from **18** and 4-chlorophenol and purified by recrystallisation from EtOH to give colourless crystals (0.76 g, 54%): thermal transitions (°C): K 78.8 (N 75.3) I (Found: C, 76.13; H, 7.12; N, 3.13; Cl, 7.58%. $C_{30}H_{34}ClNO_2$ requires C, 75.69; H, 7.20; N, 2.94; Cl, 7.45%); ν(thin film)/cm^{-1} 2222 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.20–1.60 (14H, m), 1.74–1.86 (4H, m), 3.94 (2H, d, *J* 7), 4.03 (2H, d, *J* 7), 6.83 (2H, d, *J* 9), 7.02 (2H, d, *J* 9), 7.24 (2H, d, *J* 9), 7.55 (2H, d, *J* 9), 7.66 (2H, d, *J* 9), 7.72 (2H, d, *J* 9); *m*/*z* (CI) 495 (M$^+$ + NH$_4^+$ + 2), 493 (M$^+$ + NH$_4^+$), 477 (M$^+$ + 2), 475 (M$^+$).

4-[11-(4-Bromophenyloxy)undecyloxy]-4′-cyanobiphenyl 20

The product was obtained from **18** and 4-bromophenol and purified by recrystallisation from CH$_2$Cl$_2$–EtOH to give colourless crystals (0.80 g, 53%): thermal transitions (°C): K 92.2 N 99.5 I (Found: C, 69.03; H, 6.63; N, 2.51; Br, 15.32%. $C_{30}H_{34}BrNO_2$ requires C, 69.23; H, 6.58; N, 2.69; Br, 15.35%); ν(thin film)/cm^{-1} 2220 (CN); δ_H (CDCl$_3$, 300 MHz, 25 °C) 1.30–1.60 (14H, m), 1.78–1.88 (4H, m), 3.94 (2H, d, *J* 7), 4.04 (2H, d, *J* 7), 6.81 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.39 (2H, d, *J* 9), 7.55 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m*/*z* (CI) 539 (M$^+$ + NH$_4^+$ + 2), 537 (M$^+$ + NH$_4^+$), 523 (M$^+$ + 2), 521 (M$^+$).

4-[11-(4-Cyanophenyloxy)undecyloxy]-4′-cyanobiphenyl 21

The product was obtained from **18** and 4-cyanophenol and purified by recrystallisation from EtOH–CH_2Cl_2 to give colourless crystals (0.75 g, 63%): mp = 111.2 °C (Found: C, 80.07; H, 7.28; N, 6.13%. $C_{31}H_{34}N_2O_2$ requires C, 79.80; H, 7.34; N, 6.00%); ν(thin film)/cm^{-1} 2223 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.25–1.55 (14H, m), 1.78–1.88 (4H, m), 3.98–4.08 (4H, m), 6.97 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.58 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m/z* (CI) 484 (M^+ + NH_4^+), 566 (M^+).

4-[11-(4-Methoxyphenyloxy)undecyloxy]-4′-cyanobiphenyl 22

The product was obtained from **18** and 4-methoxyphenol and purified by recrystallisation from EtOH to give colourless crystals (0.84 g, 63%): thermal transitions (°C): K 90.6 (N 78.9) I (Found: C, 79.28; H, 7.89; N, 2.91%. $C_{31}H_{37}NO_3$ requires C, 78.95; H, 7.91; N, 2.97%); ν(thin film)/cm^{-1} 2225 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.30–1.60 (14H, m), 1.73–1.88 (4H, m), 3.79 (3H, s), 3.93 (2H, t, *J* 7), 4.02 (2H, t, *J* 7), 6.85 (4H, s), 7.02 (2H, d, *J* 9), 7.55 (2H, d, *J* 9), 7.66 (2H, d, *J* 9), 7.72 (2H, d, *J* 9); *m/z* (CI) 489 (M^+ + NH_4^+), 472 (M^+).

4-[11-(4-Ethylphenyloxy)undecyloxy]-4′-cyanobiphenyl 23

The product was obtained from **18** and 4-ethylphenol and purified by recrystallisation from EtOH to give colourless crystals (0.89 g, 70%): thermal transitions (°C): K 79.0 (N 61.4) I (Found: C, 81.52; H, 7.95; N, 3.06%. $C_{32}H_{39}NO_2$ requires C, 81.84; H, 8.37; N, 2.98%); ν(thin film)/cm^{-1} 2226 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.25 (3H, t, *J* 8), 1.30–1.60 (14H, m), 1.75–1.90 (4H, m), 2.62 (2H, q, *J* 8), 3.97 (2H, t, *J* 7), 4.05 (2H, t, *J* 7), 6.86 (2H, d, *J* 9), 7.02 (2H, d, *J* 9), 7.14 (2H, d, *J* 9), 7.56 (2H, d, *J* 9), 7.68 (2H, d, *J* 9), 7.74 (2H, d, *J* 9); *m/z* (CI) 487 (M^+ + NH_4^+), 469 (M^+).

4-[11-(4-Propylphenyloxy)undecyloxy]-4′-cyanobiphenyl 24

The product was obtained from **18** and 4-propylphenol and purified by recrystallisation from EtOH to give colourless crystals (0.77 g, 57%): thermal transitions (°C): K 64.2 (N 59.5) I (Found: C, 81.77; H, 8.65; N, 2.93%. $C_{33}H_{41}NO_2$ requires C, 81.94; H, 8.54; N, 2.90%); ν(thin film)/cm^{-1} 2229 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.96 (3H, t, *J* 7), 1.30–1.70 (16H, m), 1.74–1.91 (4H, m), 2.56 (2H, t, *J* 8), 3.97 (2H, t, *J* 7), 4.04 (2H, t, *J* 7), 6.85 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.12 (2H, d, *J* 9), 7.56 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9); *m/z* (CI) 501 (M^+ + NH_4^+), 483 (M^+).

4-[11-(4-Butylphenyloxy)undecyloxy]-4′-cyanobiphenyl 25

The product was obtained from **18** and 4-butylphenol and purified by recrystallisation from EtOH–CH_2Cl_2 to give colourless crystals (0.68 g, 47%): thermal transitions (°C): K 60.5 N 67.5 I (Found: C, 82.33; H, 8.68; N, 2.66%. $C_{34}H_{43}NO_2$ requires C, 82.05; H, 8.71; N, 2.81%); ν(thin film)/cm^{-1} 2231 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.95 (3H, t, *J* 7), 1.30–1.60 (18H, m), 1.74–1.90 (4H, m), 2.58 (2H, t, *J* 8), 3.97 (2H, t, *J* 7), 4.05 (2H, t, *J* 7), 6.85 (2H, d, *J* 9), 7.03 (2H, d, *J* 9), 7.11 (2H, d, *J* 9), 7.57 (2H, d, *J* 9), 7.67 (2H, d, *J* 9), 7.73 (2H, d, *J* 9), (4H, m); *m/z* (CI) 516 (M^+ + NH_4^+), 497 (M^+).

4-[6-(4-Vinylphenyloxy)hexyloxy]-4′-*n*-propylbiphenyl 5 (n = 6)

To a solution of methyltriphenylphosphonium bromide (3.5 g, 9.8 mmol) and potassium *tert*-butoxide (1.1 g, 9.8 mmol) in THF (50 ml), a solution of **8** (n = 6) (2.7 g, 6.5 mmol) in THF (15 ml) was added dropwise. After stirring for 1 h, the solvent was removed under reduced pressure. The solid residue was purified by column chromatography (eluent: toluene) and by recrystallisation from EtOH to give colourless crystals (2.21 g, 82%): mp 132 °C (Found: C, 84.3; H, 8.25%. $C_{29}H_{34}O_2$ requires C, 84.0; H, 8.25%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.92 (3H, t, *J* 7), 1.4–2.1 (10H, m), 2.62 (2H, t, *J* 7), 4.0–4.2 (4H, m), 5.11 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.8–7.0 (4H, m), 7.21 (2H, d, *J* 9), 7.34 (2H, d, *J* 9), 7.50 (4H, m); *m/z* (CI) 414 (M^+).

The following compounds were prepared using a similar procedure.

4-[11-(4-Vinylphenyloxy)undecyloxy]-4′-*n*-propylbiphenyl 5 (n = 11)

The product was obtained from **8** (n = 11) and was purified by recrystallisation from EtOH to give colourless crystals (5.51 g, 84%): mp 78 °C (Found: C, 83.8; H, 9.3%. $C_{34}H_{44}O_2$ requires C, 84.5; H, 9.15%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.92 (3H, t, *J* 7), 1.1–2.1 (20H, m), 2.62 (2H, t, *J* 7), 4.0–4.2 (4H, m), 5.11 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.8–7.0 (4H, m), 7.21 (2H, d, *J* 9), 7.34 (2H, d, *J* 9), 7.50 (4H, m); *m/z* (CI) 502 (M^+ + NH_4^+), 485 (M^+).

4-[6-(4-Vinylphenyloxy)hexyloxy]-4′-((*S*)-(+)-2-methylbutyl)-biphenyl 6 (n = 6)

The product was obtained from **9** (n = 6) and was purified by recrystallisation from EtOH to give colourless crystals (1.53 g, 86%): mp 113 °C (Found: C, 84.55; H, 8.4%. $C_{31}H_{38}O_2$ requires C, 84.1; H, 8.65); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.90–0.93 (6H, m), 1.1–2.0 (11H, m), 2.39 (1H, q, *J* 7), 2.67 (1H, q, *J* 7), 4.0–4.2 (4H, m), 5.11 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.90 (4H, m), 7.18 (2H, d, *J* 9), 7.33 (2H, d, *J* 9), 7.50 (4H, m); *m/z* (CI) 460 (M^+ + NH_4^+), 443 (M^+).

4-[11-(4-Formylphenyloxy)undecyloxy]-4′-((*S*)-(+)-2-methylbutyl)-biphenyl 6 (n = 11)

The product was obtained from **9** (n = 11) and was purified by recrystallisation from EtOH to give colourless crystals (1.86 g, 83%): mp 67 °C (Found: C, 84.2; H, 9.7%. $C_{36}H_{48}O_2$ requires C, 84.3; H, 9.45); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.90–0.93 (6H, m), 1.1–2.0 (21H, m), 2.39 (1H, q, *J* 7), 2.67 (1H, q, *J* 7), 4.0–4.2 (4H, m), 5.10 (1H, d, *J* 11), 5.60 (1H, d, *J* 18), 6.67 (1H, dd, *J* 11,18), 6.90 (4H, m), 7.19 (2H, d, *J* 9), 7.33 (2H, d, *J* 9), 7.48 (4H, m); *m/z* (CI) 530 (M^+ + NH_4^+), 513 (M^+).

Di-{4-[11-(4-vinylphenoxy)undecyloxy]phenoxy}terephthalate 12

To a solution of terephthaloyl chloride (0.48 g, 2.4 mmol) in 1,2-dimethyloxyethane (10 ml) was added dropwise a solution of **10** (1.98 g, 5.2 mmol) and pyridine (0.75 g, 9.4 mmol) in 1,2-dimethyloxyethane (20 ml). The mixture was heated to reflux and stirred for 72 h. On cooling, the mixture was filtered and the solvent removed under reduced pressure. The solid residue was purified by column chromatography (eluent: toluene) and by repeated precipitation from CH_2Cl_2 solution by the addition of EtOH to give a white powder (0.97 g, 46%): thermal transitions: K 105 N 145 I (Found: C, 77.6; H, 8.15%. $C_{58}H_{70}O_8$ requires C, 77.8; H, 7.9); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–2.0 (36H, m), 4.0–4.2 (8H, m), 5.17 (2H, d, *J* 11), 5.63 (2H, d, *J* 18), 6.71 (2H, dd, *J* 11,18), 6.90 (8H, m), 7.19 (4H, d, *J* 9), 7.39 (4H, d, *J* 9), 8.38 (4H, s); *m/z* (EI) 849 (M^+).

The following compound was prepared using a similar procedure.

Di-{2(3)-methyl-4-[11-(4-vinylphenoxy)undecyloxy]phenoxy} terephthalate 13

The product was obtained from **11** and was purified by recrystallisation from EtOH to give colourless crystals (3.83 g, 77%): thermal transitions: K 72.8 N 107.6 I (Found: C, 77.9; H, 8.15%. $C_{60}H_{74}O_8$ requires C, 78.5; H, 8.1); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–2.0 (36H, m), 2.22 and 2.25 (6H, s), 4.0–4.2 (8H, m), 5.17 (2H, d, *J* 11), 5.63 (2H, d, *J* 18), 6.69 (2H, dd, *J* 11,18), 6.90 (6H, m), 7.15 (4H, d, *J* 9), 7.39 (4H, d, *J* 9), 8.39 (4H, s); *m*/*z* (CI) 941 ($M^+ + NH_4^+$), 923 (M^+).

Poly(4-[11-(4-vinylphenyloxy)undecyloxy]-4’-cyanobiphenyl) 14 (*n* = 11)

To a Pyrex glass ampoule was added **1** ($n = 11$) (0.5 g, 1.1 mmol), AIBN (1.5 mg, 7.8×10^{-3} mol), anhydrous THF (1.5 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 two further times. 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 light petroleum (bp 60–80) and the crude product was collected by filtration. The polymer was purified by repeated precipitation from THF solution by adding to light petroleum until no significant amount of monomer (*i.e.* less than 1%) was observed by ^{1}H NMR spectroscopy. The polymer was obtained as a white powder (200 mg, 40%): $M_n = 64 \times 103$ (average DP = 140); $M_w/M_n = 2.2$; thermal transitions (°C): G 12 S 114 I (Found: C, 81.9; H, 7.85; N, 3.0%. $C_{32}H_{37}NO_2$ requires C, 82.2; H, 8.0; N, 3.0%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–1.9 (21H, br m), 3.9–4.1 (4H, br m), 6.2–6.7 (4H, br m), 6.97 (2H, d, *J* 9), 7.51 (2H, d, *J* 9), 7.61 (4H, m).

The following polymers were prepared using a similar procedure.

Poly(4-[4-(4-vinylphenyloxy)butyloxy]-4’-cyanobiphenyl) 14 (*n* = 4)

From **1** ($n = 4$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (50 mg, 5%): $M_n = 37 \times 10^3$ (average DP = 102); $M_w/M_n = 2.2$; thermal transition: G 77 I (Found: C, 80.7; H, 6.6; N, 4.1%. $C_{25}H_{23}NO_2$ requires C, 81.25; H, 6.30; N, 3.80%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–1.9 (7H, br m), 3.9–4.1 (4H, br m), 6.2–6.8 (4H, br m), 6.92 (2H, br s), 7.42 (2H, br s), 7.60 (4H, br s).

Poly(4-[5-(4-vinylphenyloxy)pentyloxy]-4′-cyanobiphenyl) 14 (*n* = 5)

From **1** ($n = 5$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (40 mg, 13%): $M_n = 62 \times 10^3$ (average DP = 161); $M_w/M_n = 2.2$; thermal transition: G 59 I (Found: C, 81.7; H, 6.4; N, 3.5%. $C_{26}H_{25}NO_2$ requires C, 81.4; H, 6.6; N, 3.65%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–1.9 (9H, br m), 3.9–4.1 (4H, br m), 6.1–6.7 (4H, br m), 6.82 (2H, d, *J* 9), 7.38 (2H, d, *J* 9), 7.61 (4H, m).

Poly(4-[6-(4-vinylphenyloxy)hexyloxy]-4′-cyanobiphenyl) 14 (*n* = 6)

From **1** ($n = 6$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (290 mg, 58%): $M_n = 35 \times 10^3$ (average DP = 88); $M_w/M_n = 1.9$; thermal transitions (°C): G 40 S 110 I (Found: C, 81.5; H, 7.3; N, 3.3%. $C_{27}H_{27}NO_2$ requires C, 81.6; H, 6.85; N, 3.55%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–1.9 (11H, br m), 3.9–4.1 (4H, br m), 6.1–6.8 (4H, br m), 6.95 (2H, d, *J* 9), 7.44 (2H, d, *J* 9), 7.61 (4H, m).

Poly(4-[7-(4-vinylphenyloxy)heptyloxy]-4′-cyanobiphenyl) 14 (*n* = 7)

From **1** ($n = 7$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (170 mg, 57%): $M_n = 16 \times 10^3$ (average DP = 40); $M_w/M_n = 1.7$; thermal transitions (°C): G 28 S 79 I (Found: C, 80.95; H, 7.7; N, 3.15%. $C_{28}H_{29}NO_2$ requires C, 81.7; H, 7.1; N, 3.4%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.1–1.9 (13H, br m), 3.9–4.1 (4H, br m), 6.1–6.8 (4H, br m), 6.99 (2H, d, *J* 9), 7.51 (2H, d, *J* 9), 7.63 (4H, m).

Poly(4-[8-(4-vinylphenyloxy)octyloxy]-4′-cyanobiphenyl) 14 (*n* = 8)

From **1** ($n = 8$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (50 mg, 50%): $M_n = 51 \times 10^3$ (average DP = 120); $M_w/M_n = 1.7$; thermal transitions (°C): G 20 S 108 I (Found: C, 81.6; H, 7.15; N, 3.2%. $C_{29}H_{31}NO_2$ requires C, 81.85; H, 7.35; N, 3.3%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–1.9 (15H, br m), 3.9–4.1 (4H, br m), 6.2–6.8 (4H, br m), 6.96 (2H, d, *J* 9), 7.49 (2H, d, *J* 9), 7.61 (4H, m).

Poly(4-[9-(4-vinylphenyloxy)nonyloxy]-4′-cyanobiphenyl) 14 (*n* = 9)

From 1 ($n = 9$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (603 mg, 64%): $M_n = 51 \times 10^3$ (average DP = 120); $M_w/M_n = 1.7$; thermal transitions (°C): G 19 S 114 I (Found: C, 81.78; H, 7.72; N, 3.17%. $C_{30}H_{33}NO_2$ requires C, 81.97; H, 7.57; N, 3.19%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–1.9 (17H, br m), 3.9–4.1 (4H, br m), 6.15–6.75 (4H, br m), 6.96 (2H, d, *J* 9), 7.49 (2H, d, *J* 9), 7.61 (4H, m).

Poly(4-[10-(4-vinylphenyloxy)decyloxy]-4′-cyanobiphenyl) 14 (*n* = 10)

From **1** ($n = 1$) and purified by reprecipitation from CH_2Cl_2 solution into EtOH (500 mg, 46%): $M_n = 51 \times 10^3$ (average DP = 120); $M_w/M_n = 1.7$; thermal transitions (°C): G 18 S 118 I (Found: C, 81.56; H, 7.74; N, 2.98%. $C_{31}H_{35}NO_2$ requires C, 82.08; H, 7.78; N, 3.09%); ν(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$, 300 MHz, 25 °C) 1.2–1.9 (19H, br m), 3.9–4.1 (4H, br m), 6.2–6.8 (4H, br m), 6.96 (2H, d, *J* 9), 7.49 (2H, d, *J* 9), 7.61 (4H, m).

Poly(4-[6-(4-vinylphenyloxy)hexyloxy]-4′-*n*-propylbiphenyl) 15 (*n* = 6)

From **5** ($n = 6$) and purified by reprecipitation from THF solution into light petroleum (bp 30–60 °C) (600 mg, 60%): $M_n = 48 \times 10^3$ (average DP = 116); $M_w/M_n = 2.8$; thermal transitions (°C): G 94 S 139 I (Found: C, 84.0; H, 8.2%. $C_{29}H_{34}O_2$ requires C, 83.2; H, 8.19%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.92 (3H, t, *J* 7), 1.2–1.8 (13H, br m), 2.58 (2H, br s), 3.8–4.0 (4H, br m), 6.2–6.7 (4H, br m), 6.83 (2H, d, *J* 9), 7.14 (2H, d, *J* 9), 7.38 (4H, m).

Poly(4-[11-(4-vinylphenyloxy)undecyloxy]-4′-*n*-propylbiphenyl) 15 (*n* = 11)

From **5** ($n = 11$) and purified by reprecipitation from THF solution into light petroleum (bp 30–60 °C) (270 mg, 27%): $M_n = 70 \times 10^3$ (average DP = 144); $M_w/M_n = 2.8$; thermal transition (°C): S 118 I (Found: C, 83.8; H, 9.6%. $C_{29}H_{34}O_2$ requires C, 84.25; H, 9.15%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.92 (3H, t, *J* 7), 1.1–1.8 (23H, br m), 2.58 (2H, br s), 3.8–4.0 (4H, br m), 6.2–6.7 (4H, br m), 6.85 (2H, d, *J* 9), 7.18 (2H, d, *J* 9), 7.41 (4H, m).

Poly(4-[6-(4-vinylphenyloxy)hexyloxy]-4′-((*S*)-(+)-2-methylbutyl)-biphenyl) 16 (*n* = 6)

From **6** ($n = 6$) and purified by reprecipitation from THF solution into light petroleum (bp 30–60 °C) (153 mg, 17%): $M_n = 40 \times 10^3$ (average DP = 90); $M_w/M_n = 4.32$; thermal transition (°C): S 68 I (Found: C, 83.65; H, 8.8%. $C_{31}H_{38}O_2$ requires C, 84.1; H, 8.65%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.89 (6H, br m), 1.1–1.8 (14H, br m), 2.26 (1H, br m), 2.54 (1H, br m), 3.7–4.0 (4H, br m), 6.2–6.7 (4H, br m), 6.80 (2H, d, *J* 9), 7.04 (2H, d, *J* 9), 7.36 (4H, m).

Poly(4-[11-(4-vinylphenyloxy)undecyloxy]-4′-((*S*)-(+)-2-methylbutyl)biphenyl) 16 (*n* = 11)

From **6** ($n = 11$) and purified by reprecipitation from THF solution into light petroleum (bp 30–60 °C) (350 mg, 35%): $M_n = 21 \times 10^3$ (average DP = 41); $M_w/M_n = 2.1$; thermal transitions (°C): G 30 S 88 I (Found: C, 84.5; H, 9.55%. $C_{36}H_{48}O_2$ requires C, 84.3; H, 8.45%); δ_H ($CDCl_3$, 300 MHz, 25 °C) 0.88 (6H, br m), 1.0–1.8 (24H, br m), 2.33 (1H, br m), 2.61 (1H, br m), 3.7–4.0 (4H, br m), 6.2–6.7 (4H, br m), 6.89 (2H, d, *J* 9), 7.12 (2H, d, *J* 9), 7.40 (4H, m).

Acknowledgements

We thank EPSRC for CASE studentships (A. C. and S. B.) and Merck Speciality Chemicals Ltd., NB-SC for funding.

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