Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Boden, N. , Bushby, R. J. and Lu, Z. B.(1998) 'A rational synthesis of polyacrylates with discogenic side groups', Liquid Crystals, 25: 1, 47 — 58

To link to this Article: DOI: 10.1080/026782998206489

URL: http://dx.doi.org/10.1080/026782998206489

Liquid Crystals, 1998, Vol. 25, No. 1, 47–58

A rational synthesis of polyacrylates with discogenic side groups

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(*Received 17 October 1997; in final form 8 December 1997; accepted 31 January 1988*)

The ferric chloride mediated oxidative coupling of 3,3′,4,4′-tetrahexyloxybiphenyl with 2-hexyloxyanisole followed by demethylation gave 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene. Reaction with *tert*-butyldimethylsilyl-protected 6-bromohexanol, removal of the protecting group, and condensation with acryloyl chloride or methacryloyl chloride gave acrylate and methacrylate monomers with hexamethylene 'spacers'. Alternatively, reaction of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene with 2-(2-chloroethoxy)ethanol followed by acryloyl chloride or methacryloyl chloride gave acrylate and methacrylate monomers with diethylenoxy 'spacers'. Both of the poly(acrylate) homopolymers and the poly(methacrylate) homopolymer with the diethylenoxy 'spacer' gave columnar liquid crystal phases. This is contrary to the current perception that the methacrylate polymer backbone is too inflexible to be incorporated in columnar phases.

1. Introduction

The unique supramolecular architecture of the columnar phases of discotic liquid crystal materials, together with their surface-alignment and electrical conductivity properties make them potentially applicable in areas as diverse as information storage [1], sensors [2], displays [3] and high-resolution xerography [4]. Many of these potential applications require thin film preparations with good mechanical properties—almost certainly thin films of *polymeric* discotic liquid crystals. Thin films of polymeric discotic liquid crystals are more difficult to align than their low molar mass counterparts, but a number of solutions to this problem have been described [5–7]. Finklemann and co-workers [5] have demonstrated that polymeric discotic liquid crystalline films can be aligned by stretching, and that the alignment of weakly cross-linked material can be stabilized by further cross-linking. Ultraviolet irradiation of a film of acrylate monomers containing a trace of a photosensitive initiator and aligned by surface forces has been shown to give aligned films of polymer [6]. Furthermore, the Langmuir–Blodgett technique has been used by Ringsdorf *et al.* [7] to produce multilayers of polymeric triphenylene discotics in which the columns lie parallel to the surface.

The most widely synthesized and studied low molar mass discotic liquid crystals are the hexa-alkoxy and hexa-acyloxy derivatives of triphenylene [8]. Routes to equivalent triphenylene-based discotic liquid crystalline polymers were first pioneered by Ringsdorf and co-workers [5, 9]. The key step in their syntheses was the partial alkylation of 2,3,6,7,10,11-hexahydroxybenzene which was followed by a chromatographic separation of the products. It is a route which produces the requisite monofunctional and bifunctional triphenylenes, but is one which, because of the chromatographic step, is difficult to apply on more than a limited scale. Furthermore, the bifunctional monomers obtained by this route (the monomers required for making 'main-chain' discotic polymers) are an inseparable mixture of isomers leading to polydisperse products. We subsequently developed a 'rational', non-statistical route to unsymmetrically substituted derivatives of triphenylene in which the key step is the ferric chloride mediated coupling of an alkoxybenzene to an alkoxybiphenyl followed by a reductive work-up [10, 11]. This reaction can be used to prepare relatively large amounts of pure (single isomer) monomers. In a previous paper we described the application of this methodology to the preparation of *main chain* discotic liquid crystal polymers [11]. In this paper, we describe its application to the preparation of *side group* discotic liquid crystal polymers. Acrylate/methacrylate-based monomers were chosen [12, 13] so as to make use of the ultraviolet irradiation initiated polymerization route for making aligned polymeric films [6].

2. Results

2.1. *Synthesis and properties of the monomers*

Four kinds of monofunctional triphenylene-based discotic liquid crystalline monomers **6–9** have been synthesized according to the method shown in scheme 1.

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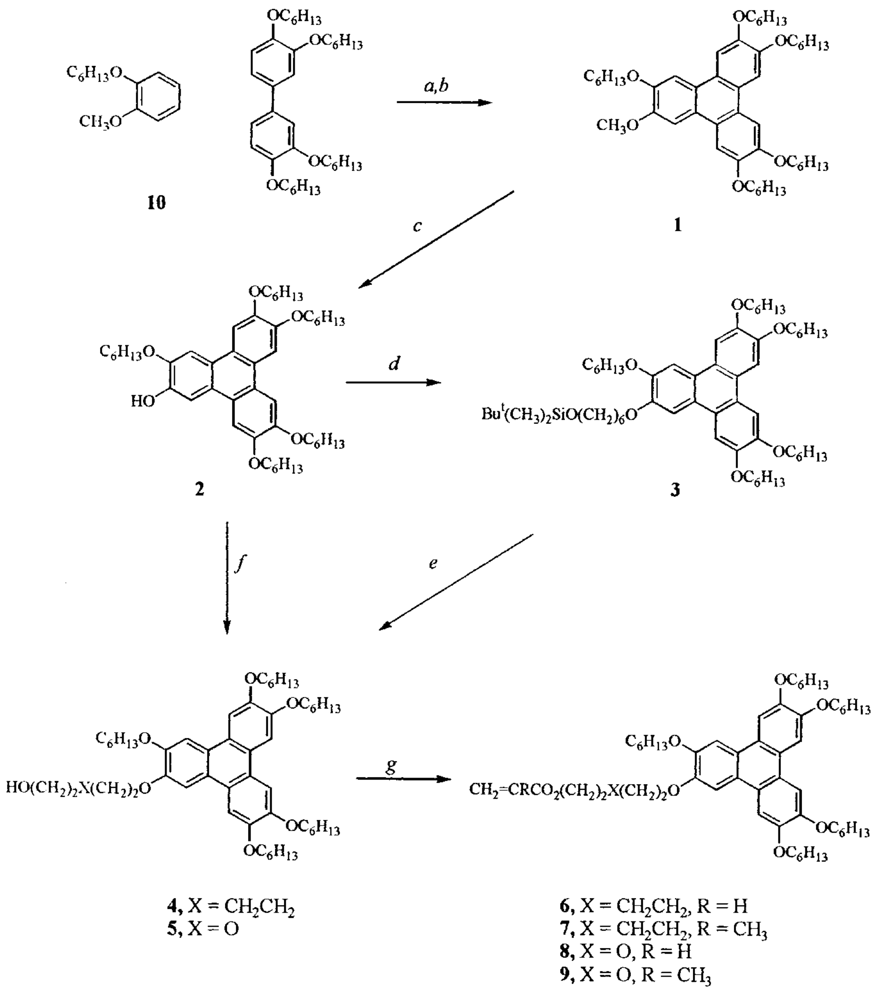


Scheme 1. (*a*) $FeCl_3/CH_2Cl_2$, (*b*) MeOH/61% (two steps), (*c*) Ph_2PLi/THF/0°C/69%, (*d*) $Bu^tMe_2SiO(CH_2)_6Br/K_2CO_3$/EtOH, (*e*) $Bu_4N^+F^-$/THF/50°C/64% (two steps), (*f*) $HOCH_2CH_2OCH_2CH_2Cl/K_2CO_3$/EtOH/43%, (*g*) $CH_2{=}CHCOCl$ or $CH_2{=}CMeCOCl/Pr^i_2EtN/CH_2Cl_2$/0°C/76–89%.

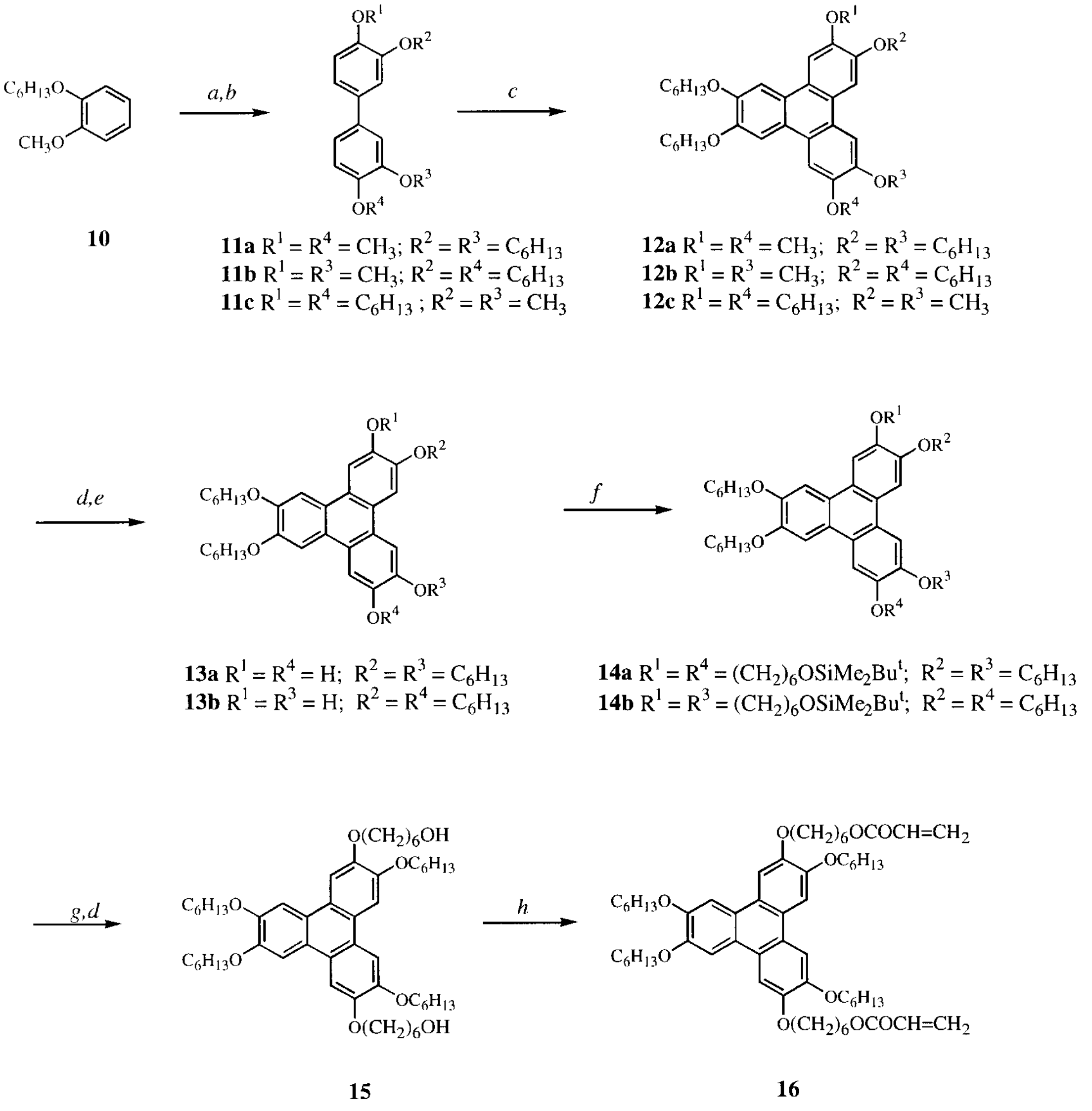
The synthesis of a bifunctional monomer **16** is shown in scheme 2 and that of a trifunctional monomer **20** in scheme 3.

3,6,7,10,11-Pentahexyloxy-2-methoxytriphenylene **1** (scheme 1) was prepared using the ferric chloride mediated coupling of tetrahexyloxybiphenyl with 2-hexyloxyanisole [10, 11]. This was then converted to 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **2** using diphenylphosphenyl lithium. The free hydroxyl group in compound **2** was alkylated using 1-bromo-6-(*tert*-butyldimethylsilyloxy)hexane or 2-(2-chloroethoxy)ethanol to give (after removal of the silyl protecting group from compound **3** [14]) two intermediates 3,6,7,10,11-pentahexyloxy-2-(6-hydroxyhexyloxy)triphenylene **4** and 2-[2-(2-hydroxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene **5**. Finally, the free hydroxyl groups in these intermediates were esterified using methacryloyl chloride or acryloyl chloride to give four monomers **6**–**9**. The intention in making all four of these monomers was to gain some insight into the relative virtues of the two different polymer backbones (polyacrylate and polymethacrylate) and of the two spacers (hexamethylene and diethylenoxy). The polymer backbones differ in their flexibility and glass transition temperatures. The spacers also differ in their flexibility and conformational behaviour. In this respect it is interesting to compare the ^1H NMR spectra of the monomers. Whereas the aromatic hydrogens in monomers **6** and **7** are all equivalent, one of the aromatic hydrogens in monomers **8** and **9**, presumably the one *ortho* to the ethylenoxy chain, is deshielded by 0·1 ppm. The simplest explanation of this difference is that it arises from different shielding contributions from different side chain conformations. The monomers **6**, **8** and **9** and the intermediates **4** and **5** all give columnar mesophases as detailed in table 1. Compared with symmetrically substituted hexahexyloxytriphenylenes their mesomorphic temperature ranges are reduced.

Table 1. Mesomorphic behaviour of the monomers: transition temperatures (DSC onset temperatures) and enthalpies in parenthesis.

Monomer	Phase transitions (heating)/°C (/J g^{-1})	Phase transitions (cooling)/°C (/J g^{-1})
4	Cr 62 (40) Col 67 (4) I	I 65 (−4) Col 43 (−38) Cr
5	Cr 60 (22) Col$_1$ 66 (19) Col$_2$ 78 (4) I	I 73 (−4) Col 36 (−43) Cr
6	Cr 46 (52) I	I 44 (−3) Col 31 (−46) Cr
7	Cr 48 (47) I	I 30 (−43) Cr
8	Cr 48 (40) Col 64 (3) I	I 60 (−3) Col 29 (−40)
9	Cr 45 (38) Col 56 (2) I	I 56 (−2) Col 24 (−34)

Since the bifunctional and trifunctional monomers **16** and **20** were only required for use on a small scale (as added cross-linking agents) it proved economic to use 'statistical' coupling routes and to separate the required isomers by chromatography. The route to monomer **16** is a variant of a route to a similar monomer previously reported by Ringsdorf and co-workers [13] except that the chain lengths differ as does the separation method.



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11a $R^1 = R^4 = CH_3$; $R^2 = R^3 = C_6H_{13}$
11b $R^1 = R^3 = CH_3$; $R^2 = R^4 = C_6H_{13}$
11c $R^1 = R^4 = C_6H_{13}$; $R^2 = R^3 = CH_3$

12a $R^1 = R^4 = CH_3$; $R^2 = R^3 = C_6H_{13}$
12b $R^1 = R^3 = CH_3$; $R^2 = R^4 = C_6H_{13}$
12c $R^1 = R^4 = C_6H_{13}$; $R^2 = R^3 = CH_3$

13a $R^1 = R^4 = H$; $R^2 = R^3 = C_6H_{13}$
13b $R^1 = R^3 = H$; $R^2 = R^4 = C_6H_{13}$

14a $R^1 = R^4 = (CH_2)_6OSiMe_2Bu^t$; $R^2 = R^3 = C_6H_{13}$
14b $R^1 = R^3 = (CH_2)_6OSiMe_2Bu^t$; $R^2 = R^4 = C_6H_{13}$

15 **16**

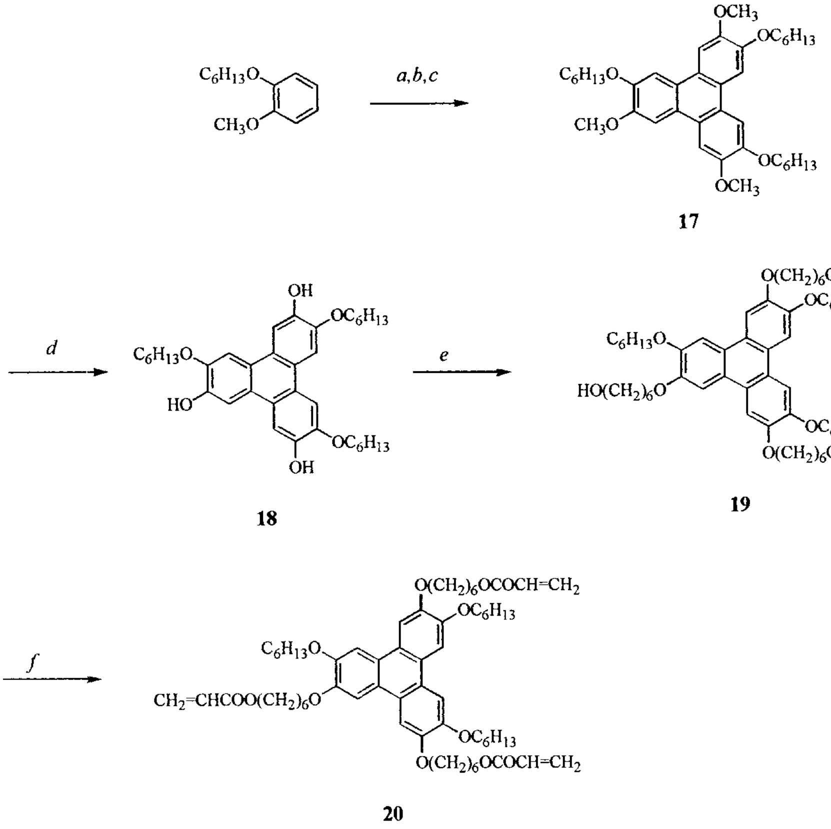
Scheme 2. (*a*) ICl, (*b*) Cu/Δ, (*c*) $FeCl_3/CH_2Cl_2$ followed by MeOH/26%, (*d*) chromatographic separation of isomers, (*e*) Ph_2PLi/THF/0°C/51%, (*f*) $Bu^tMe_2SiO(CH_2)_6Br/K_2CO_3$/EtOH, (*g*) $Bu_4N^+F^-$/THF/50°C/23% (two steps), (*h*) $CH_2{=}CHCOCl/Pr^i_2EtN/CH_2Cl_2$/0°C/91%.

The ferric chloride mediated coupling of 1,2-dihexyloxybenzene with the mixture of dihexyloxydimethoxybiphenyls **11a**–**11c** (scheme 2) gave a mixture of three products **12a**–**12c**. The 2,7-dimethoxy isomer **12a** is the most desirable intermediate since only the product **16** derived from this isomer is likely to be free of the problems of intramolecular reactions between two acryloyl residues [11]. By chromatography it is easy to separate the 3,6-isomer **12c** as a pure fraction, but the required 2,7-isomer **12a** is obtained as a mixed fraction contaminated by the 2,6-isomer **12b**. This mixture of isomers was carried through the next three steps (demethylation, realkyation and deprotection) and only at this stage was it easy to separate the isomers by chromatography. The synthesis was then completed through the acylation of the purified diol **15**.

The synthesis of the trifunctional monomer **20** (scheme 3) relied on the ferric chloride mediated trimerization of methoxyhexyloxybenzene. A mixture of two isomers was obtained. The symmetrical isomer (2,6,10-trimethoxy) is the minor product and cannot be satisfactorily made in this way [13, 15], but the unsymmetrically substituted isomer **17** is easily separated from the mixture [16]. It was elaborated into the trisacrylate **20** by the method shown.

2.2. *Synthesis and properties of the polymers*

For convenience, the homopolymers made from monomers **6**–**9** are referred to as polymers **poly-6**, **poly-7** etc. These polymers were prepared through an AIBN initiated free radical polymerization of solutions of each of the monomers **6**–**9** in benzene and were purified by reprecipitation. A random copolymer was prepared by copolymerization of monomer **6** with methyl acrylate (weight ratio 50:50, molar ratio 9:91). This copolymer is referred to as **copoly-6-a**. Its composition, revealed by ^{1}H NMR and by combustion analysis, corresponded closely to the molar ratio of monomers used. Cross-linked copolymers were also prepared using a 95:5 weight ratio of the monomers **6** and **16** (**copoly-6-16**) and a 95:5 weight ratio of the monomers **6** and **20** (**copoly-6-20**). Polymer molecular masses and molecular mass distributions were measured by GPC against polystyrene standards in tetrahydrofuran and these are given in table 2. In all cases, the degree of polymerization achieved was quite modest (of the order 10–100mers).



Scheme 3. (*a*) $FeCl_3/CH_2Cl_2$, (*b*) MeOH/, (*c*) chromatographic separation of isomers (27% two steps and chromatography), (*d*) $Ph_2PLi/THF/0°C/72\%$, (*e*) $Bu^tMe_2SiO(CH_2)_6Br/K_2CO_3/EtOH$ followed by $Bu_4N^+F^-/THF/50°C/76\%$, (*f*) $CH_2{=}CHCOCl/Pr^i_2EtN/CH_2Cl_2/0°C/48\%$.

Table 2. Molecular mass data for the polymers.

Polymer	M_n	M_w	M_n/M_w
poly-6	$6\cdot05\times10^{3}$	$7\cdot35\times10^{3}$	1·21
poly-7	$9\cdot84\times10^{4}$	$1\cdot48\times10^{5}$	1·50
poly-8	$7\cdot65\times10^{3}$	$8\cdot96\times10^{3}$	1·17
poly-9	$6\cdot79\times10^{3}$	$8\cdot89\times10^{3}$	1·31
copoly-6-a	$2\cdot64\times10^{4}$	$5\cdot77\times10^{4}$	2·19
copoly-6-16	$3\cdot47\times10^{4}$	$8\cdot98\times10^{4}$	2·59
copoly-6-20	$5\cdot8\times10^{4}$	$9\cdot4\times10^{4}$	1·6

Note that there was a small but significant improvement in the molecular masses when the cross-linking agents **16** and **20** were added to the monomer **6**. Transition temperatures and DSC data for the polymers are given in table 3. The clearing points of the polymers are 30–50°C higher than those for the corresponding monomers. The enthalpies associated with the melting of **poly-6**, **poly-8**, and **poly-9** are 1–2 J g^{-1}, of the order expected for a Col–I transition in the polymer. Low angle X-ray diffraction, for **poly-6**, **poly-8**, and **poly-9** below the Col–I transition temperature shows a single diffraction peak corresponding to the 19 Å column–column separation expected for a columnar phase. No additional diffraction peaks were observed. Thin film preparations of **poly-6**, **poly-8**, and **poly-9** are birefringent giving a 'speckled' texture similar to that observed for main chain discotic liquid crystalline polymers (see the figure) [11]. Together, these lines of evidence show the liquid crystalline nature of the phase [5, 9, 11, 12].

It is interesting to compare each of the monomers with the corresponding polymer. In terms of transition temperatures and enthalpies the differences are not very great and, in terms of X-ray diffraction, the Col phases of the polymers and monomers are almost indistinguishable. It is tempting to argue that, given that the space between the columns in the Col phase is filled with disordered chains, it does not matter if, as in the polymer, some of these are linked together. However, optical microscopy shows that the monomers and the polymers are very different. The figure shows a comparison between typical optical textures for thin-film preparations of the monomer **8** and of the corresponding polymer **poly-8**, both as first obtained on cooling from the isotropic melt into the Col phase. The greater 'grain/domain' sizes are immediately apparent. Furthermore, the dynamics of the systems are very different. When thin film preparations of the monomers are annealed just below the Col–I transition temperature, a homeotropic film is obtained over a period of a few minutes. Similar behaviour is found for the corresponding oligomeric systems [17]. However, even when the polymers are annealed a few degrees below the Col–I transition temperature for a month there is no obvious change in the texture; a homeotropic film is not obtained.

Cross-linking of the polymer **6** using the difunctional and trifunctional additives **16** and **20** increases the molecular masses (table 2), but it also destroys the liquid crystalline behaviour. No birefringence was observed for **copoly-6-16** and **copoly-6-20** or for **poly-7** and **copoly-6-a**. These amorphous/isotropic materials did not melt below 200°C.

3. Discussion

It is interesting to compare the properties of these new polymers with those reported by Werth and Spiess [12]. These authors prepared the monomers **21** and **22** by the 'Ringsdorf' route [9]. AIBN initiated polymerization in butan-2-one gave homopolymers with weight-average molecular masses greater than 10^{6}. **Poly-21** gave a columnar phase described as 'highly distorted hexagonal' Col 39°C I (T_g, -8°C) with a column–column separation of 19·4 Å, whereas **poly-22** proved to be amorphous. The failure of this polymethacrylate to give a columnar phase was attributed to the fact that the glass transition for the polymethacrylate

Table 3. Mesomorphic behaviour and low angle X-ray diffraction data for the polymers. Transition temperatures were determined by polarizing microscopy, and glass transition temperatures and transition enthalpies (in parenthesis) by DSC.

Polymer	Phase transitions (heating)/°C (/J g^{-1})	Phase transitions (cooling)/°C	Column–column distance in the Col phase/Å	T_g °C
poly-6	Col 84 (1) I	I 45 Col	19·0	5
poly-7	no transitions up to 200°C[a]	—	—	
poly-8	Col 117 (2) I	I 101 Col	19·0	
poly-9	Col 110 (2) I	I 89 Col	19·0	
copoly-6	no transitions up to 200°C[a]	—	—	
copoly-6-16	no transitions up to 200°C[a]		–	
copoly-6-20	no transitions up to 200°C[a]		—	

[a] Isotropic, non-birefringent materials which soften and become relatively easy to shear at 50–60°C, but which show no DSC transitions up to 200°C.

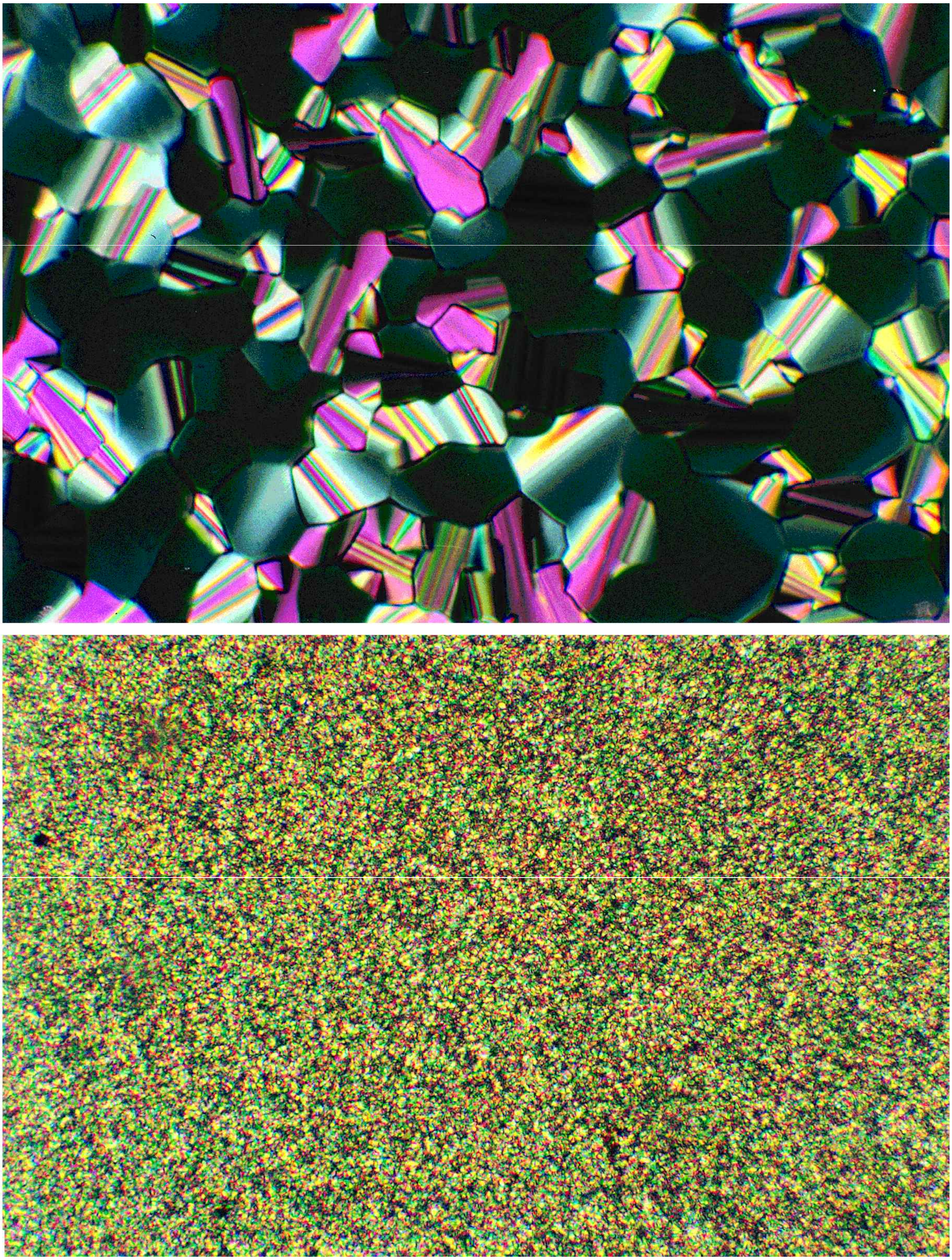
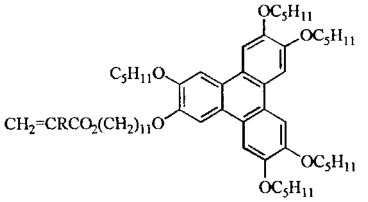


Figure 1. A comparison of the optical microscopic textures of the monomer **8** (upper) and the corresponding polymer **poly-8** (lower), both immediately after cooling from the isotropic liquid into the columnar phase and both shown at the same magnification.

backbone is higher than that for the polyacrylate backbone, making it insufficiently flexible to be readily accommodated within the mesophase structure. Our polymers differ from those prepared by Werth and Spiess in being based on hexyloxytriphenylene rather than pentyloxytriphenylene substituents, in employing $(CH_2)_6$ or $(CH_2)_2O(CH_2)_2$ 'spacers' rather than $(CH_2)_{11}$ 'spacers', and in being of lower molecular mass.



21, R = H
22, R = CH_3

As Werth and Speiss point out, polymers are unlikely to give a Col_h phase below the glass transition of the polymer backbone and the ability to form the Col_h phase may be compromised at temperatures just above T_g. Although this may be a significant factor for some polymethacrylates, it clearly depends on the structure, the particular T_g and mesophase ranges involved. Glass transition temperatures for polymethacrylates decrease with increasing chain length in the side group. The methyl ester has $T_g = 105°C$, the pentyl ester $-5°C$ and the decyl ester $-70°C$ [18]. Furthermore, for chains longer than *ca.* C_{12}, T_g starts to rise again and values for polymethacrylates lie below those of the corresponding polyacrylates [18]. The T_g values are little affected by 'oxa' substitution [18], but are quite strongly dependent on the degree of polymerization [19]. In comparing **poly-7** and **poly-22** with **poly-9** it could be argued that **poly-9** is the only one to give a columnar phase because its relatively low degree of polymerization leads to a low T_g [19]. However, reasonable estimates of the effect of molecular mass on T_g [19] suggest that, even at very high molecular masses, T_g for **poly-9** would lie well below the Col/I transition temperature of 110°C and that DP is unlikely to be an issue. In comparing **poly-7** and **poly-9** the more significant factor is probably the difference in behaviour of the monomers. Monomer **9** gives a columnar phase, but monomer **7** does not.

The reason for some of the low molecular masses and for the wide range of molecular masses apparent in table 2 is not entirely clear, but it probably reflects different polymer solubility limits in the solvents used.

4. Conclusion

A rational synthesis of discotic side group columnar liquid crystal polymers based on poly(methacrylate) and poly(acrylate) backbones has been developed. This new synthesis uses a minimal amount of chromatography and, at least in principle, is easier to scale up than the 'Ringsdorf' route. DSC, X-ray diffraction and optical microscopy show that three of the homopolymers made exhibit columnar liquid crystalline phases. Contrary to previous work, both polyacrylate and polymethacryate backbones have been successfully exploited. In general, only the lower molecular mass products display mesomorphic behaviour. Cross-linking of the polymers results in loss of the liquid crystalline behaviour.

5. Experimental

5.1. *General procedures*

^1H NMR spectra were recorded on GE QE300 instruments using $CDCl_3$ as solvent. Mass spectra were obtained on a VG Autospec Instrument. Phase behaviour was studied using an Olympus BH-2 optical polarizing microscope with a Mettler FP82 HT hot stage and a Perkin-Elmer 7 thermal analysis system (cooling and heating rate, 10°C min^{-1}). Small angle X-ray diffraction experiments were conducted with a pinhole camera consisting of a Phillips generator and tubes, nickel-filtered Cu K_α radiation of wavelength $\lambda = 0{\cdot}154$ nm, and a Lindemann sample tube (0·7 mm i.d.) to plate distance of 112·8 mm. Gel permeation chromatography was performed on two mixed bed columns (Polymer Laboratories Ltd) using a Merck L-6000 pump and a Varex light-scattering detector. Tetrahydrofuran (HPLC grade) was used as an eluent at a flow rate of 1 ml min^{-1}. Molecular masses are reported relative to two narrow polystyrene standards.

5.2. *Syntheses*

5.2.1. *2-Hexyloxyanisole*

Guaiacol (124 g, 1 mol) was alkylated with 1-bromohexane (198 g, 1·2 mol) and potassium carbonate (278 g, 2·0 mol) in boiling ethanol (200 ml) to give 2-hexyloxyanisole (175 g, 82%) as a colourless liquid (b.p. 175°C/1 mm Hg). Elemental analysis: C 74·9, H 9·9; $C_{13}H_{20}O_2$ requires C 75·0, H 9·62%. Mass spectrum: *m/z* (EI) 208 (M^+, 22%). ^1H NMR: δ_H ($CDCl_3$) 0·91 (3H, t, $J = 6{\cdot}9$ Hz, CH_2CH_3), 1·33–1·46 (6H, m, $OCH_2CH_2(CH_2)_3$), 1·84 (2H, m, OCH_2CH_2), 3·84 (3H, s, Ar–OCH_3), 4·00 (2H, t, $J = 6{\cdot}8$ Hz, OCH_2), and 6·95 (4H, s, ArH).

5.2.2. *3,6,7,10,11-Pentahexyloxy- 2-methoxytriphenylene* **1**

3,3′,4,4′-Tetrahexyloxybiphenyl (6·0 g, 11·0 mmol), ferric chloride (7·13 g, 44·0 mmol, 4 equiv.) and 2-hexyloxyanisole (4·58 g, 22·0 mmol, 2 equiv.) were added to dichloromethane (100 ml), stirred at room temperature. The reaction was monitored by TLC. When the reaction had finished, the mixture was carefully poured into methanol (300 ml) and cooled to 0°C. The crude product was filtered off, purified by column chromatography (silica eluting with dichloromethane : petroleum ether, 3 : 2), and recrystallized from ethanol to give 3,6,7,10,11-pentahexyloxy-2-methoxytriphenylene **1** (5 g, 61%, m.p. 79°C). Elemental analysis: C 77·8, H 9·9; $C_{49}H_{74}O_6$ requires C 77·53, H 9·82%. Mass spectrum: *m/z* (FAB) 758 (M^+, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·95 (15H, t, $J = 6{\cdot}8$ Hz, CH_2CH_3), 1·35-1·50 (30H, m, $OCH_2CH_2(CH_2)_3$), 1·95 (10H, m, OCH_2CH_2), 4·05 (3H, s, OCH_3), 4·23 (10H, t, $J = 6{\cdot}5$ Hz, OCH_2), 7·82 (6H, s, ArH).

5.2.3. *3,6,7,10,11-Pentahexyloxy-2-hydroxytriphenylene* **2** [17]

Diphenylphosphine [20] (2·6 ml, 15 mmol) was added to dried tetrahydrofuran (100 ml) under argon at 0°C; butyllithium solution in hexane (10 ml, 1·6M, 16 mmol) was then added dropwise over 30 min with stirring. After another 30 min, 3,6,7,10,11-pentahexyloxy-2-methoxytriphenylene **1** (7·25 g, 9·56 mmol) was added and the mixture heated under reflux. When the reaction had finished (TLC), the mixture was poured onto ice, and the organic matter extracted with dichloromethane. The organic phase was washed with aqueous hydrochloric acid (2M) and water, dried and the solvents removed *in vacuo*. The crude product was subjected to column chromatography (silica eluting with dichloromethane : petroleum ether, 1 : 1), and recrystallized from ethanol to give white crystals of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene (4·89 g, 69%). Elemental analysis: C 77·6, H 9·7; $C_{48}H_{72}O_6$ requires C 77·38, H 9·74%. Mass spectrum: *m/z* (EI) 744 (M^+, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·95 (15H, t, $J = 9{\cdot}4$ Hz, CH_2CH_3), 1·35–1·50 (30H, m, $OCH_2CH_2(CH_2)_3$), 1·95 (10H, m, OCH_2CH_2), 4·10 (10H, t, $J = 6{\cdot}0$ Hz, OCH_2), 5·85 (1H, s, OH), 7·72 (1H, s, ArH), 7·80 (4H, s, ArH), 7·90 (1H, s, ArH).

5.2.4. *1-Bromo-6-(tert-butyldimethylsilyloxy)hexane* [14]

6-Bromohexanol (5 g), *tert*-butyldimethylsilyl chloride (5·32 g, 1·2 equiv.), triethylamine (7·67 ml, 2·0 equiv.) and 4-dimethylaminopyridine (0·334 g, 0·099 equiv.) were added to dichloromethane (25 ml). The mixture was stirred for 11 h at room temperature during which time a white precipitate formed. Ether (150 ml) was added to the mixture, the solution was washed with one portion of water (80 ml), and the aqueous layer shaken with two further portions of ether (60 ml). The combined organic extracts were washed with water (60 ml), saturated brine solution (80 ml), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The crude product was subjected to column chromatography (silica eluting with 5% ethyl acetate/hexane) to give 1-bromo-6-(*tert*-butyldimethylsilyloxy)hexane (7·19 g, 88%, b.p. 96–98°C/0·85 mm Hg). ^{1}H NMR: δ_H: ($CDCl_3$) 0·05 (6H, s, $Si(CH_3)_2$), 0·89 (9H, s, $SiC(CH_3)_3$), 1·35–1·55 (6H, m, $BrCH_2(CH_2)_3$), 1·85 (2H, m, CH_2CH_2OSi), 3·40 (2H, t, $J = 6{\cdot}8$ Hz, $BrCH_2$), 3·61 (2H, t, $J = 6{\cdot}3$ Hz, $SiOCH_2$).

5.2.5. *3,6,7,10,11-Pentahexyloxy-2-(6-hydroxyhexyloxy)-triphenylene* **4**

A mixture of 3,6,7,10,11-pentahexyloxy-2-hydroxytriphenylene **2** (3·53 g, 4·74 mmol), 1-bromo-6-(*tert*-butyldimethylsilyloxy)hexane (1·68 g, 5·69 mmol, 1·2 equiv.), potassium carbonate (2·61 g, 19·0 mmol, 4·0 equiv.) in ethanol (50 ml) was heated under reflux for 27 h until the reaction finished (monitored by TLC and by following the disappearance of the OH signal in the ^{1}H NMR). The mixture was treated with dichloromethane and the extracts dried over magnesium sulphate, filtered and evaporated *in vacuo*. The crude silylated intermediate **3** was dissolved in tetrahydrofuran (93 ml, to give a solution of 0·05 M) and tetrabutylammonium fluoride solution in tetrahydrofuran (14 ml, 1M, 2 equiv. per silyl group) was added. The reaction mixture was heated to 50°C for 2 h and left stirring overnight at room temperature. Dichloromethane was added and the mixture washed with water. The organic phase was dried with magnesium sulphate, filtered and evaporated *in vacuo*. The crude product was subjected to column chromatography (silica eluting with dichloromethane : ethyl acetate 3 : 2); ethanol was added to initiate crystallization to give the product **4** as white crystals (2·58 g, 64%). Elemental analysis: C 76·7, H 9·9; $C_{54}H_{84}O_7$ requires C 76·74, H 10·01%. Mass spectrum: *m/z* (EI) 826 ($[M–H_2O]^+$, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·92 (15H, t, $J = 6{\cdot}5$ Hz, CH_2CH_3), 1·39–1·59 (36H, m, $OCH_2CH_2(CH_2)_3$), 1·93 (12H, m, OCH_2CH_2), 3·65 (2H, t, $J = 6{\cdot}3$ Hz, CH_2OH), 4·21 (12H, t, $J = 6{\cdot}5$ Hz, OCH_2), 7·81 (6H, s, ArH).

5.2.6. *2-[2-(2-Hydroxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene* **5**

A mixture of 3,6,7,10,11-pentahexyloxy-2-hydroxy-triphenylene **2** (3·8 g, 5·11 mmol), 2-(2-chloroethoxy)ethanol (0·76 g, 6·13 mmol, 1·2 equiv.) and potassium carbonate (2·81 g, 20·4 mmol, 4 equiv.) in ethanol (50 ml) was heated under reflux for ten days. The mixture was treated with dichloromethane and the extracts dried with magnesium sulphate, filtered and evaporated *in vacuo*. The crude product was subjected to column chromatography (silica eluting with dichloromethane : petroleum ether 2 : 1). Ethanol was added to initiate crystallization to give white crystals of 2-[2-(2-hydroxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene **5** (1·85 g, 43%). Elemental analysis: C 75·0, H 9·5; $C_{52}H_{80}O_8$ requires C 74·96, H 9·67%. Mass spectrum: *m/z* (EI) 832 ($[M]^+$, 100%); 43($[CH{=}CHOH]^+$, 54%). ^{1}H NMR: δ_H ($CDCl_3$)

0·93 (15H, t, $J = 6{\cdot}8$ Hz, $\mathrm{CH_2}\mathit{CH_3}$), 1·35–1·58 (30H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·9 (10H, t, $J = 6{\cdot}5$ Hz, $\mathrm{OCH_2}\mathit{CH_2}$), 3·80 (4H, $\mathrm{O}\mathit{CH_2CH_2}\mathrm{OH}$), 4·02 (2H, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{O}$), 4·23 (10H, t, $J = 6{\cdot}2$ Hz, $\mathrm{O}\mathit{CH_2}$), 4·41 (2H, t, $J = 4{\cdot}2$ Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2O}$), 7·90 (1H, s, ArH) and 7·83 (5H, s, Ar–H).

5.2.7. *2-[(6-Methacryloyloxy)hexyloxy]-3,6,7,10,11-pentahexyloxytriphenylene* **7**

Methacryloyl chloride (0·157 g, 1·5 mmol) was added to the mixture of 2-(6-hydroxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (0·844 g, 1 mmol), di-isopropylethylamine (0·195 g, 1·5 mmol) and 2,6-di-*tert*-butyl-*para*-cresol (35 mg) in dichloromethane (20 ml) at 0°C under nitrogen. The reaction mixture was stirred for 2 h at room temperature and washed with aqueous potassium carbonate. The organic phase was dried over magnesium sulphate, filtered and concentrated *in vacuo*. The crude methacrylate was purified by column chromatography (silica eluting with dichloromethane). Methanol was added to initiate crystallization to give the pure product **7** (0·70 g, 76%) as white crystals. Elemental analysis: C 76·2, H 9·7; $\mathrm{C_{58}H_{88}O_8}$ requires C 76·28, H 9·71%. Mass spectrum: *m/z* (FAB), 913 ($[\mathrm{M}+1]^+$, 100%). ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·92 (15H, t, $J = 6{\cdot}7$ Hz, $\mathrm{CH_2}\mathit{CH_3}$), 1·40–1·57 (36H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·93 (15H, m, $\mathrm{OCH_2}\mathit{CH_2}$ and $\mathit{CH_3}\mathrm{–C{=}CH_2}$), 4·21 (12H, t, $J = 6{\cdot}4$ Hz, $\mathrm{Ar–OCH_2}$ and 2H, m, $\mathit{CH_2}\mathrm{OCO}$), 5·50 and 6·07 (2H, C= $\mathit{CH_2}$, s), 7·81 (6H, br. s, ArH). Like the other acrylate and methacrylate monomers this could be satisfactorily stored in this form at 0°C for several weeks.

5.2.8. *2-[(6-Acryloyloxy)hexyloxy]-3,6,7,10,11-pentahexyloxytriphenylene* **6**

In a similar manner to **7**, 2-(6-acryloyloxy)-hexyloxy-3,6,7,10,11-pentahexyloxytriphenylene was prepared (0·8 g, 89%). Elemental analysis: C 75·95, H 9·9; $\mathrm{C_{57}H_{86}O_8}$ requires C 76·13, H 9·63%. Mass spectrum: *m/z* (FAB), 899 ($[\mathrm{M}+1]^+$, 100%). ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·93 (15H, t, $J = 6{\cdot}8$ Hz, $\mathrm{CH_2}\mathit{CH_3}$), 1·40–1·60 (36H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·95 (12H, m, $\mathrm{OCH_2}\mathit{CH_2}$), 4·24 (12H, t, $J = 6{\cdot}5$ Hz, $\mathrm{Ar\text{-}O}\mathit{CH_2}$ and 2H, m, $\mathit{CH_2}\mathrm{OCO}$), 5·81 (1H, d, $J = 10$ Hz, $\mathrm{CH{=}CH}\mathit{H}$), 6·07 (1H, dd, $J = 10$ and 16 Hz, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$) 6·37 (1H, d, $J = 16$ Hz, $\mathrm{CH{=}CH}\mathit{H}$) and 7·81 (6H, br. s, ArH).

5.2.9. *2-[2-(2-Acryloyloxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene* **8**

In a similar manner to **7**, 2-[2-(2-acryloyloxyethoxy)-ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene was synthesized (0·76 g, 85%). Elemental analysis: C 74·45, H 9·40; $\mathrm{C_{55}H_{82}O_9}$ requires C 74·46, H 9·31%. Mass spectrum: *m/z* (FAB), 886 ($[\mathrm{M}]^+$, 100%). ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·93 (15H, t, $J = 6{\cdot}8$ Hz, $\mathrm{CH_2}\mathit{CH_3}$), 1·40–1·58 (30H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·94 (10H, m, $\mathrm{OCH_2}\mathit{CH_2}$), 3·92 (2H, t, $J = 4{\cdot}6$ Hz, $\mathrm{–O}\mathit{CH_2}\mathrm{CH_2O–}$), 4·01 (2H, t, $J = 4{\cdot}8$ Hz, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{O}$), 4·23 (10H, t, $J = 6{\cdot}4$ Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2O}$), 4·39 (4H, m, $\mathrm{ArO}\mathit{CH_2}\mathrm{CH_2O}$ and $\mathit{CH_2}\mathrm{OCO–CH{=}CH_2}$), 5·79 (1H, d, $J = 10$ Hz, $\mathrm{CH{=}CH}\mathit{H}$), 6·15 (1H, dd, $J = 10$ and 16 Hz, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$) 6·40 (1H, d, $J = 16$ Hz, $\mathrm{CH{=}CH}\mathit{H}$), and 7·83 (5H, s, ArH), 7·90 (1H, s, ArH).

5.2.10 *2-[2-(2-Methacryloyloxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene* **9**

In a similar manner, 2-[2-(2-methacryloyloxyethoxy)-ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene (0·79 g, 87%) was prepared. Elemental analysis: C 74·65, H 9·50; $\mathrm{C_{56}H_{84}O_9}$ requires C 74·63, H 9·39%. Mass spectrum: *m/z* (FAB), 901 ($[\mathrm{M}+1]^+$, 100%). ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·93 (15H, t, $J = 6{\cdot}8$ Hz, $\mathrm{CH_2}\mathit{CH_3}$), 1·40–1·63 (30H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·94 (13H, m, $\mathrm{OCH_2}\mathit{CH_2}$ and $\mathit{CH_3}\mathrm{–C{=}CH_2}$), 3·92 (2H, t, $J = 4{\cdot}4$ Hz, $\mathit{CH_2}\mathrm{CH_2O}$), 4·01 (2H, t, $J = 4{\cdot}2$ Hz, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{O}$), 4·23 (10H, t, $J = 6{\cdot}1$ Hz, $\mathrm{O}\mathit{CH_2}$), 4·39 (4H, m, $\mathrm{ArO}\mathit{CH_2}\mathrm{CH_2O}$ and $\mathit{CH_2}\mathrm{OCO–C(CH_3){=}CH_2}$), 5·53 (1H, s, C= $\mathit{CH_2}$), 6·13 (1H, s, C= $\mathit{CH_2}$), 7·83 (5H, s, ArH), 7·90 (1H, s, ArH).

5.2.11. *Dihexyloxydimethoxybiphenyl mixed isomers* **11a-11c**

The mixture of isomers was prepared from 2-hexyloxyanisole (52 g, 0·25 mol) by iodination and Ullmann coupling following the same procedure as for the synthesis of 3,3′,4,4′-tetrahexyloxybiphenyl [10, 11, 17] (yield 13·5 g, 26%). ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·90 (6H, m, $\mathrm{CH_2}\mathit{CH_3}$), 1·35–1·50 (12H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·85 (4H, m, $\mathrm{OCH_2}\mathit{CH_2}$), 3·85 (6H, m, $\mathrm{O}\mathit{CH_3}$), 3·92 (4H, m, $\mathrm{O}\mathit{CH_2}$), 6·89 (4H, m, ArH), 7·06 (2H, br. s, ArH).

5.2.12. *Tetrahexyloxydimethoxytriphenylene mixed isomers* **12a-12c**

The mixture of dihexyloxydimethoxybiphenyl isomers **11a-11c** (13·5 g) was reacted with 1,2-dihexyloxybenzene **10** (12 g, 1·2 equiv.) under the conditions described in §5.2.2. Column chromatography (on silica eluting with dichloromethane:petroleum ether, 2:1) gave 2,7,10,11-tetrahexyloxy-3,6-dimethoxytriphenylene **12c** (5·2 g, 23%, $R_\mathrm{f} = 0{\cdot}40$) [13] and the mixed 2,7- and 2,6-dimethoxy isomers **12a** and **12b** of which the 2,7-dimethoxy isomer was the main component (5·47 g, 24%, $R_\mathrm{f} = 0{\cdot}50$) [13]. For isomers **12a** and **12b.** ^{1}H NMR: δ_H ($\mathrm{CDCl_3}$) 0·94 (12H, m, $\mathrm{CH_2}\mathit{CH_3}$), 1·40–1·58 (24H, m, $\mathrm{OCH_2CH_2}(\mathit{CH_2})_3$), 1·95 (8H, m, $\mathrm{OCH_2}\mathit{CH_2}$), 4·10 (6H, s, $\mathrm{ArO}\mathit{CH_3}$), 4·25 (8H, m, $\mathrm{ArO}\mathit{CH_2}$), 7·81 (6H, m, $\mathrm{Ar}\mathit{H}$).

5.2.13. *Tetrahexyloxy-2,7- and -2,6-dihydroxy-triphenylenes **13a**, **13b***

A mixture of tetrahexyloxy-2,7- and -2,6-dimethoxy-triphenylenes **12a** and **12b** (5·47 g, 7·94 mmol), butyllithium (14·9 ml in hexane, 23·8 mmol, 3 equiv.) and diphenylphosphine lithium (4·14 ml, 23·8 mmol, 3 equiv.) in tetrahydrofuran was heated under reflux until the cleavage of the two methoxy groups was complete (monitored by TLC and ^{1}H NMR). When the reaction had finished, the mixture was poured onto ice and the organic material extracted with dichloromethane. The organic phase was washed with aqueous hydrochloric acid (2M) and water, dried, filtered and concentrated under reduced pressure. The crude product was subjected to column chromatography (silica eluting with dichloromethane: petroleum ether, 2:1), and recrystallized from ethanol to give a white crystalline product which was a mixture of tetrahexyloxy-2,7- and -2,6-dihydroxytriphenylene **13a** and **13b** (3·1 g, 51%). ^{1}H NMR: δ_H ($CDCl_3$) 0·95 (12H, br. s, CH_2CH_3), 1·35–1·50 (24H, m, $CH_2(CH_2)_3CH_3$), 1·95 (8H, br. m, OCH_2CH_2), 4·10 (8H, m, OCH_2CH_2), 5·85 (2H, br. s, OH), 7·72 (4H, br. s, ArH), 7·80 (2H, br. s, ArH).

5.2.14. *3,6,10,11-Tetrahexyloxy-2,7-bis(6-hydroxy-hexyloxy)triphenylene **15***

A mixture of tetrahexyloxy-2,7- and -2,6-dihydroxy-triphenylene **13a** and **13b** (3·10 g, 4·69 mmol), 1-bromo-6-(*tert*-butyldimethylsilyloxy)hexane (3·32 g, 11·2 mmol, 2·4 equiv.) and potassium carbonate (2·59 g, 19·0 mmol) in ethanol (50 ml) was heated under reflux for 27 h until the reaction was complete (monitored by TLC and ^{1}H NMR until the OH signal had disappeared). The mixture was shaken with dichloromethane and the extracts dried with magnesium sulphate. The crude mixture of silylated products **14a** and **14b** was dissolved in tetrahydrofuran (65 ml, to give a *ca.* 0·05M solution) and tetrabutylammonium fluoride (28 ml in tetrahydrofuran, 1M, 2 equiv. per silyl group) was added. The reaction mixture was heated at 50°C for 2 h and stirred at room temperature overnight. Dichloromethane was added and the mixture washed with water. The organic phase was dried with magnesium sulphate, filtered and evaporated. The crude product was subjected to column chromatography (on silica eluting with dichloromethane: ethyl, acetate 3:2); ethanol was added to initiate crystallization to give 3,7,10,11-tetrahexyloxy-2,6-bis(6-hydroxyhexyloxy)-triphenylene (0·15 g, 4% over two steps, m.p. 72·5°C) and 3,6,10,11-tetrahexyloxy-2,7-bis(6-hydroxyhexyloxy)-triphenylene **15** (0·93 g, 23% over two steps, m.p. 82°C). The two isomers were readily distinguished by ^{1}H NMR spectroscopy since isomer **15** possesses an additional plane of symmetry.

For 3,6,10,11-tetrahexyloxy-2,7-bis(6-hydroxyhexyloxy)-triphenylene **15**. Elemental analysis: C 75·2, H 9·8; $C_{54}H_{84}O_8$ requires C 75·31, H 9·83%. Mass spectrum: *m/z* (EI) 860 ($[M]^+$, 46%). ^{1}H NMR: δ_H ($CDCl_3$) 0·93 (12H, t, $J = 6{\cdot}5$ Hz, CH_2CH_3), 1·40–1·60 (36H, m, $OCH_2CH_2(CH_2)_3$), 1·94 (12H, m, OCH_2CH_2), 3·69 (4H, br. m, CH_2OH) 4·23 (12H, t, $J = 6{\cdot}2$ Hz, $ArOCH_2$), 7·83 (6H, s, ArH).

5.2.15. *2,7-Bis[(6-acryloyloxy)hexyloxy]-3,6,10,11-tetrahexyloxytriphenylene **16***

Acryloyl chloride (0·157 g, 1·5 mmol) was added to the mixture of 2,7-bis(6-hydroxyhexyloxy)-3,6,10,11-tetrahexyloxytriphenylene **15** (0·430 g, 0·5 mmol), di-isopropylethylamine (0·195 g, 1·5 mmol) and 2,6-di-*tert*-butyl-*para*-cresol (35 mg) in dichloromethane (20 ml) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 2 h at room temperature and washed with dilute aqueous potassium carbonate. The organic phase was dried with magnesium sulphate, filtered and evaporated. The crude acrylate was purified by column chromatography (on silica eluting with dichloromethane). Methanol was added to initiate crystallization to give the pure product **16** (0·44 g, 91%, m.p. 41°C). Elemental analysis: C 74·5, H 8·95; $C_{60}H_{88}O_{10}$ requires C 74·34, H 9·15%. Mass spectrum: *m/z* (EI), 968 ($[M]^+$, 6%). ^{1}H NMR: δ_H ($CDCl_3$) 0·93 (12H, br. s, CH_2CH_3), 1·40–1·75 (36H, m, $OCH_2CH_2(CH_2)_3$), 1·94 (12H, m, OCH_2CH_2), 4·23 (16H, br. s, OCH_2 and CH_2OCO), 5·83 (1H, d, $J = 10$ Hz, CH=CHH), 6·13 (1H, dd, $J = 10$ and 16 Hz, CH=CH$_2$) 6·38 (1H, d, $J = 16$ Hz, CH=CHH), 7·83 (6H, s, ArH).

5.2.16. *3,6,11-Trihexyloxy-2,7,10-trimethoxytriphenylene **17***

This was prepared by trimerization of 2-hexyloxy-anisole (20 g) using ferric chloride in the manner described in § 5.2.2. The product was obtained following column chromatography (on silica eluting with dichloromethane: petroleum ether, 4:1), and recrystallized from ethanol to give compound **17** as white crystals (5·3 g, 27%, m.p. 102°C, lit. [16] 100°C). Elemental analysis: C 75·65, H 8·9; $C_{39}H_{54}O_6$ requires C 75·7, H 8·79%. Mass spectrum: *m/z* (EI) 618 ($[M]^+$, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·95 (9H, t, $J = 6{\cdot}5$ Hz, CH_2CH_3), 1·41–1·57 (18H, m, $-OCH_2CH_2(CH_2)_3$), 1·98 (6H, t, $J = 6{\cdot}9$ Hz, OCH_2CH_2), 4·10 (9H, s, OCH_3), 4·26 (6H, t, $J = 6{\cdot}8$ Hz, OCH_2), 7·78 (6H, s, ArH). The identification of this as the unsymmetrically substituted isomer rests in part on its melting point, but also on the lack of symmetry displayed in the ^{1}H NMR spectrum of its demethylation product **18**.

5.2.17. *3,6,11-Trihexyloxy-2,7,10-trihydroxytriphenylene* ***18***

In a similar manner to that described in § 5.2.3, the 3,6,11-trihexyloxy-2,7,10-trimethoxytriphenylene **17** was demethylated to give the trihydroxy compound **18** (2.08 g, 72%, m.p. 164–169°C). Elemental analysis: C 75·05, H 8·25; $C_{36}H_{48}O_6$ requires C 74·97, H 8·39%. Mass spectrum: *m/z* (FAB), 576 ($[M]^+$, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·94 (9H, m, CH_2CH_3), 1·20–1·65 (18H, m, $OCH_2CH_2(CH_2)_3$), 1·92 (6H, m, OCH_2CH_2), 4·23 (6H, m, OCH_2), 7·66 (1H, s, ArH), 7·67 (1H, s, ArH), 7·75 (1H, s, ArH), 7·91 (2H, s, ArH), 7·92 (1H, s, ArH).

5.2.18. *3,6,11-Trihexyloxy-2,7,10-tris(6-hydroxyhexyloxy)triphenylene* ***19***

In a similar manner to that described in § 5.2.5, 3,6,11-trihexyloxy-2,7,10-trihydroxytriphenylene **18** was converted into the tris(6-hydroxyhexyloxy) product **19** (76%, m.p. 52°C). Elemental analysis: C 73·4, H 9·5; $C_{54}H_{84}O_9$ requires C 73·93, H 9·65%. Mass spectrum: *m/z* (FAB), 877 ($[M+1]^+$, 43%). ^{1}H NMR: δ_H ($CDCl_3$) 0·93 (9H, m, CH_2CH_3), 1·20–1·80 (36H, m, $OCH_2CH_2(CH_2)_3$), 1·94 (12H, m, OCH_2CH_2), 3·68 (6H, m, CH_2OH), 4·23 (12H, m, Ar–OCH_2), 7·83 (6H, s, ArH).

5.2.19. *2,7,10-Tris(6-acryloyloxyhexyloxy)-3,6,11-trihexyloxytriphenylene* ***20***

In a similar manner to that described in § 5.2.7, the 3,6,11-trihexyloxy-2,7,10-tris(6-hydroxyhexyloxy)triphenylene **19** was converted into the tri-ester **20** (48%, m.p. 38°C). Elemental analysis: C 72·85, H 8·95; $C_{63}H_{90}O_{12}$ requires C 72·80, H 8·73%. Mass spectrum: *m/z* (FAB), 1038 ($[M]^+$, 100%). ^{1}H NMR: δ_H ($CDCl_3$) 0·93 (9H, m, CH_2CH_3), 1·10–2·00 (48H, m, $OCH_2(CH_2)_4$), 4·23 (18H, m, OCH_2 and CH_2-$OCOCH{=}CH_2$), 4·23 (12H, m, OCH_2), 5·80 (1H, d, $J = 10$ Hz, $CH{=}CHH$), 6·13 (1H, dd, $J = 10$ and 16 Hz, $CH{=}CH_2$) 6·37 (1H, d, $J = 16$ Hz, $CH{=}CHH$), 7·83 (6H, s, ArH).

5.2.20. *Polymerization of 2-[2-(2-acryloyloxyethoxy)-ethoxy]-3,6,7,10,11-pentahexyloxy-triphenylene* ***8*** *to give* ***poly-8***

A mixture of 2-[2-(2-acryloyloxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene **8** (0·2 g) and AIBN (4 mg) in benzene (4 ml) was heated under reflux (60°C) for 5 days. The polymer solution was poured into a large volume of stirred methanol, the precipitate filtered off, and purified by reprecipitation from dichloromethane/methanol to give **poly-8** (0·14 g, 70%) as a grey powder. Elemental analysis: C 73·15, H 9·30; $[C_{55}H_{82}O_9]_n$ requires C 74·46, H 9·31%. ^{1}H NMR: δ_H ($CDCl_3$) 0·91 (15H, br. s, –CH_2CH_3), 1·05–2·15 (43H, br. m, Ar–$OCH_2(CH_2)_4$, and –CH–CH_2–), 3·40–4·60 (18H, br. s Ar–OCH_2 and Ar–$OCH_2CH_2OCH_2CH_2O$), 7·00–7·95 (6H, br. s, ArH).

5.2.21. *Polymerization of 2-[(6-acryloyloxy)hexyloxy]-3,6,7,10,11-pentahexyloxytriphenylene* ***6*** *to give* ***poly-6***

2-[(6-Acryloyloxy)hexyloxy]-3,6,7,10,11-pentahexyloxytriphenylene **6** was polymerized and **poly-6** was purified in a similar manner to **poly-8** to give 0·16 g, 53%. Elemental analysis: C 75·85, H 9·90; $[C_{57}H_{86}O_8]_n$ requires C 76·13, H 9·63%. ^{1}H NMR: δ_H ($CDCl_3$) 0·91 (15H, br. s, CH_2CH_3), 1·05–2·10 (51H, br. m, Ar–$OCH_2(CH_2)_4$ and –CH–CH_2–), 3·60–4·40 (12H, br. m, Ar–OCH_2), 7·50–7·90 (6H, br. s, ArH).

5.2.22. *Polymerization of 2-[(6-methacryloxy)hexanoxy]-3,6,7,10,11-pentahexyloxy-triphenylene* ***7*** *to give* ***poly-7***

In a similar manner to the above, 2-[(6-methacryloyloxy)hexyloxy]-3,6,7,10,11-pentahexyloxytriphenylene **7** was polymerized and purified (0·14 g, 46%). Elemental analysis: C 74·80, H 9·65; $[C_{58}H_{88}O_8]_n$ requires C 76·28, H 9·71%. ^{1}H NMR: δ_H ($CDCl_3$) 0·40–2·15 (68H, m, Ar–$OCH_2(CH_2)_4CH_3$, Ar–OCH_2–$(CH_2)_5$, and –$C(CH_3)$–CH_2–), 3·60–4·30 (14H, Ar–OCH_2 and CH_2OCO), 7·00–7·80 (6H, Ar–H).

5.2.23. *Polymerization of 2-[2-(2-methacryloyloxyethoxy)-ethoxy]-3,6,710,11-pentahexyloxytriphenylene* ***9*** *to* ***poly-9***

In a similar manner to the above, 2-[2-(2-methacryloyloxyethoxy)ethoxy]-3,6,7,10,11-pentahexyloxytriphenylene **9** was polymerized and purified (0·10 g, 33%). Elemental analysis: C 73·65, H 9·35; $[C_{56}H_{84}O_9]_n$ requires C 74·63, H 9·35%. ^{1}H NMR: δ_H ($CDCl_3$) 0·60–2·10 (60H, br. m, $ArOCH_2(CH_2)_4CH$ and –$C(CH_3)$–CH_2–), 3·60–4·50 (18H, br. m, $ArOCH_2$ and $ArOCH_2CH_2OCH_2CH_2O$), 7·20–7·80 (6H, br. s, ArH).

5.2.24. *Copolymerization of 2-[(6-acryloyloxy)-hexyloxy]-3,6,7,10,11-pentahexyloxy-triphenylene* ***6*** *and methyl acrylate to give* ***copoly-6-a***

A mixture of 2-[(6-acryloyloxy)hexyloxy]3,6,7,10,11-pentahexyloxy-triphenylene **6** (0·20 g), methyl acrylate (0·25 g) and AIBN (4 mg) in benzene (4 ml) was heated at 70°C under an atmosphere of nitrogen for three days; the polymer produced was precipitated with methanol and purified by reprecipitation from dichloromethane/methanol to give the white copolymer **copoly-6-a** (0·23 g). Elemental analysis: C 66·15, H 8·60%. Copolymer composition (molar % triphenylene component): 9·02% based on the microanalysis, and 8·28% based on the ^{1}H NMR ratio of aromatic to methyl signal integrations. ^{1}H NMR: δ_H ($CDCl_3$) 0·93 (br. s, CH_2CH_3), 1·1–2·5 (m, CH_2 and CH), 3·4–3·8 (br. m, OCH_3), 4·0–4·4 (m, CH_2O), 7·8 (br. s, ArH).

5.2.25. *Copolymerization of 2-(6-acryloyloxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* ***6*** *and 2,7-bis[(6-acryloyloxy)hexyloxy]-3,6,10,11-tetrahexyloxytriphenylene* ***16*** *to give* **copoly-6-16**

The mixture of 2-(6-acryloyloxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **6** (0·180 g), 2,7-bis[(6-acryloyloxy)hexyloxy]-3,6,10,11-tetrahexyloxytriphenylene **16** (0·010 g, 5% mol ratio) and AIBN (4 mg) in benzene (4 ml) was heated at 70°C under a nitrogen atmosphere for three days, then at 80°C for a further two days. The polymer was precipitated with a large volume of methanol, and purified by reprecipitation from chloroform/methanol to give **copoly-6-16** (90 mg). Elemental analysis: C 75·2, H 9·45%. ^{1}H NMR: δ_H ($CDCl_3$) 0·40–2·45 (m, Ar–$OCH_2(CH_2)_4CH_3$, Ar–$OCH_2(CH)_4$ and CH–CH_2), 3·40–4·50 (m, Ar–OCH_2 and CH_2OCO), 7·10–7·90 (m, ArH).

5.2.26. *Copolymerization of 2-(6-acryloyloxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene* ***6*** *and 2,7,10-tris(6-acryloyloxyhexyloxy)-3,6,11-trihexyloxy-triphenylene* ***20*** *to give* **copoly-6-20**

The mixture of 2-(6-acryloyloxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **6** (204 mg), 2,7,10-tris(6-acryloyloxyhexyloxy)-3,6,11-trihexyloxytriphenylene **20** (26 mg) and AIBN (8 mg) in benzene (4 ml) was heated at 70°C under a nitrogen atmosphere for three days and then at 80°C for a further two days. The polymer was precipitated with a large volume of methanol, and purified by reprecipitation from chloroform/methanol to give **copoly-6-20** (90 mg). Elemental analysis: C 74·65, H 8·65%. ^{1}H NMR: δ_H ($CDCl_3$) 0·40–2·45 (m, Ar-$OCH_2(CH_2)_4CH_3$, Ar–$OCH_2(CH)_4$ and CH–CH_2), 3·40–4·50 (Ar-OCH_2 and CH_2OCO), 7·10–7·90 (m, ArH).

We thank the Overseas Research Students Awards Scheme (O.R.S.) and the University of Leeds (Tetley and Lupton Scheme) for awards to Z.L.

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