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Polycatenar oligophenylene liquid crystals

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We report the synthesis of oligophenylene polycatenar liquid crystals incorporating 1,4-disubstituted phenyl rings joined by a direct carbon carbon bond and some pyrimidine analogues. The nature of the linkages does appear to affect the mesomorphism significantly. The ratio of the aromatic core to the aliphatic chains is varied systematically by changing the number of 1,4-disubstituted phenyl rings and the length of the aliphatic chains. This strongly influences the transition temperatures of the mesophases. Some of the compounds are columnar over an extended temperature range of more than 200°C with melting points below room temperature. We suggest that a combination of the poor overlap of the conjugated electron system of the molecular cores making up the columnar structure and the high concentration of aliphatic chains leads to a low charge-carrier mobility.

1. Introduction

Polycatenar mesogens may be regarded as being dichotomous or having calamitic, rod-like and discotic characteristics and exhibit both calamitic and columnar liquid crystal phases [1–6]. Polycatenar materials consist of a long rigid rod-like central core with a high number of flexible aliphatic side chains in terminal and lateral positions. A typical polycatenar molecule comprising a rigid rod-like elongated polyaromatic and highly-conjugated core contains between four to six aromatic rings linked together in the *para*-positions by unsaturated linkages with four to six terminal aliphatic chains on the two outermost aromatic rings in a 2mp–2mp (two chains attached in the *meta–para* positions) configuration or a 3mpm–3mpm (three chains attached in the *meta–para–meta* positions) configuration, depending on the number of chains. It is also possible to form a tetracatenar arrangement of 2mm–2mm (biforked), or an unsymmetrical arrangement of 2mp–2pm. However, polycatenars with these arrangements of terminal chains are not usually liquid crystalline. The bicatenar to hexacatenar compounds give rise to a diverse range of liquid crystalline properties. When considering the tetracatenar or hexacatenar compounds it has been generally established that the presence of shorter chain lengths usually leads to the appearance of nematic and smectic C phases and the longer chain lengths give rise to columnar phases [2, 3]. Varying the chain length of polycatenar compounds can change the mesogenic behaviour from that of the calamitic rod-like materials to that of columnar materials [4].

The main factor leading to the formation of nematic and smectic phases, mainly the smectic C phase in polycatenars, is microphase separation [1–6]. This results from the fact that the aromatic cores of the neighbouring molecules are attracted to each other by van der Waals forces of attraction due to interaction between adjacent π-clouds of electron density, while the aliphatic chains are also attracted to each other. Another factor governing the mesomorphic behaviour is that in simple calamitic compounds with one or two terminal chains there is not much difference between the cross-sectional volume of the aromatic core and that of the alkyl chain region. However, where polycatenars are concerned the presence of extra aliphatic chains means that the cross-sectional area of the alkyl chains is more extensive than that of the central core resulting in a kink in the rotation volume of the compound. This non-cigar shaped rotation volume in the polycatenar materials means that the chains and the aromatic cores have to arrange themselves in the smectic C phase when the chain lengths are of an intermediate length between very short and long [1–6].

When the length of the aliphatic chains is increased then columnar mesophases are usually observed. The aromatic cores of polycatenars form self-assembled molecular aggregates of columns in a supramolecular structure. The columnar mesophases observed for polycatenars are usually made up from self-assembled slices containing a cluster of three, four or five rigid cores of the polycatenar molecules arranged side-by-side surrounded

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by a periphery of aliphatic chains leading to the formation of the columnar mesophase [6]. X-ray diffraction studies of tetracatenar compounds have shown that the columns are made up of at least four molecules grouped together. The corresponding hexacatenars aggregate to form a self-assembled column of discs made up of three molecules due to the space requirements of more chains.

It is conceivable that polycatenars could find use as hole-transport layers in multilayer organic light-emitting diodes (OLEDs) due to their self-assembled liquid crystalline structures and low ionization potential. The order in the liquid crystal state has the potential of achieving a high hole mobility present in single crystals without the traps and defects found at the crystal grain boundaries. The conductivity can be improved if the one-dimensional structure of the materials used in the hole-transport layer of the OLEDs can be drawn out into a two-dimensional structure along with increasing the order and homogeneity in the organized structure [7]. Therefore, we report measurements of the hole mobility of polycatenar liquid crystals to test this hypothesis. We also describe a systematic study of polycatenar compounds with only a direct carbon–carbon bond linking the aromatic rings in the molecular core instead of the flexible linkages, e.g. –CH=CH–, –CH=N– and –COO–, usually present in polycatenars. The number of 1,4-disubstituted rings is varied from four to six and the length and number of the alkoxy chains is varied in order to study the correlation between the size and shape of the aromatic core and the number and length of the aliphatic chains and the type of mesophase formed as the values of the liquid crystal transition temperature. We have prepared a number of oligophenylene polycatenars and several nitrogen-containing analogues to carry out these studies. Liquid crystalline 2,5-disubstituted pyrimidines can act as electron-transport layers in OLEDs [7, 8].

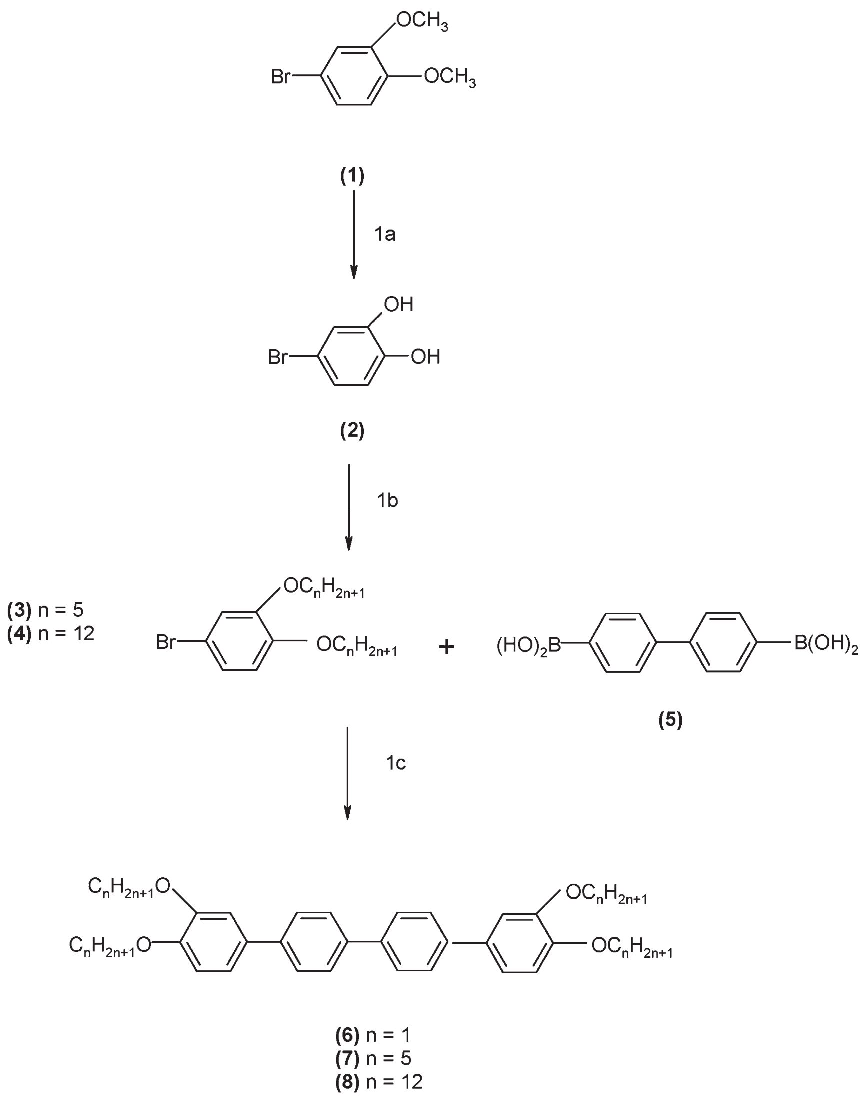
2. Experimental

2.1. *Instrumentation*

All commercially available starting materials, reagents and solvents were used as supplied (unless otherwise stated) and were obtained from Aldrich, Strem Chem. Inc, Acros or Lancaster Synthesis. All reactions were carried out using a dry nitrogen atmosphere unless water was present as solvent or reagent and the temperatures were measured internally. Mass spectra were recorded using a gas chromatography/mass spectrometer (GC/MS)-QP5050A Schimadzu with electron impact (EI) at a source temperature of 200°C. Compounds with an RMM>800 $\mathrm{g\,mol^{-1}}$ were analysed using a Bruker, reflex IV, matrix-assisted laser desorption/ionization (MALDI), time of flight (TOF) MS. A 384 well microlitre plate format was used with a scout target. Samples were dissolved in DCM with HABA [2-(4-hydroxyphenylazo)-benzoic acid] matrix (1:10, respectively). The mass ion of the material is identified by M^+. ^{1}H NMR spectra were recorded using a JEOL Lambda 400 spectrometer and an internal standard of tetramethylsilane (TMS) was used. GC was carried out using a Chromopack CP3800 gas chromatogaph equipped with a 10 m CP-SIL 5CB column. Purification of intermediates and final products was mainly accomplished by gravity column chromatography, using silica gel (40–63 μm, 60 A) obtained from Fluorochem. The purity of the final compounds was determined by elemental analysis using a Fisons EA 1108 CHN analyser. The melting point and the other transition temperatures of the solid compounds prepared were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarizing microscope. The liquid crystal transition temperatures of all of the final products were confirmed using a Perkin-Elmer DSC-7 and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the reported value of the transition temperatures. The charge carrier mobility of the hexacatenar **40** was determined by a standard photocurrent time-of-flight method [9]. A glass/ITO/film/ITO/glass cell structure was used for most samples. The cells were filled by vacuum-assisted movement of the compounds in their isotropic phase and then sealed. The thickness, l, of the thin films was 2 μm. All samples were heated to isotropic before testing and measurements were taken on cooling. An optical pulse from N_2 laser (Laser Science VSL-337ND, 337 nm) incident on the thin film creates a thin sheet of electron-hole pairs next to the contact. A uniform electric field, $E=3.3 \times 10^4\,\mathrm{V\,cm^{-1}}$, was applied across the organic layer and the transit time, τ, obtained from the intercept of the photocurrent plateau and tail, plotted on a logarithmic scale. The carrier mobility, μ, was obtained from the equation $\mu=l/(E\tau)$ [9].

2.2. *Synthesis*

The synthesis, purification and characterization of the intermediates and final products are described in detail in the supplementary information. The tetracatenar compounds **6–8** were synthesized as shown in scheme 1. The commercially available starting dimethyl ether **1** was dealkylated using boron tribromide according to a literature method [10] to yield the diphenol **2**, which was then *O*-alkylated using the appropriate alkyl bromide in a standard Williamson ether synthesis [11] to give intermediate phenyl ethers **3** and **4**. The tetracatenar compounds **6–8** were synthesized using



Scheme 1. Reagents and conditions: 1a (i) BBr_3, DCM, (ii) H_2O; 1b BrC_nH_{2n+1}, K_2CO_3, butanone; 1c $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O.

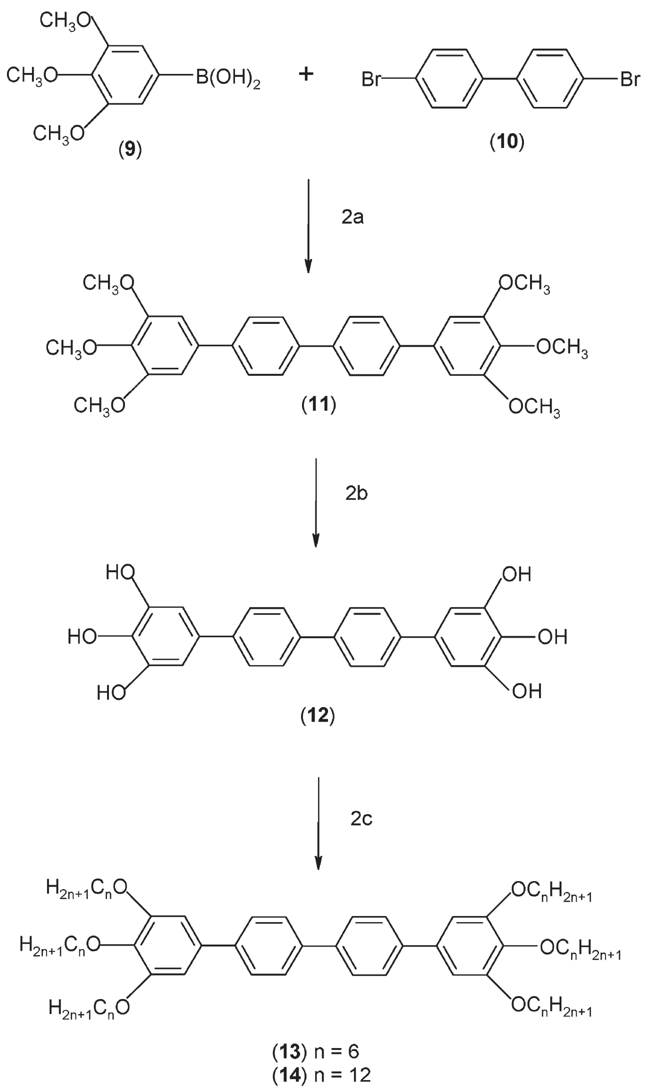
Suzuki palladium-catalysed aryl–aryl cross-coupling reactions [12–14] between the commercially available aryl boronic acid **5** and the aryl bromides **3** and **4**.

The hexacatenar compounds **11**, **13** and **14** were synthesized as shown in scheme 2. The phenylboronic acid **9** and the 4,4′′-dibromobiphenyl **10** are both commercially available and were used in a Suzuki aryl–aryl cross-coupling reaction [12–14] to yield the quaterphenyl **11**, which was demethylated in the usual way [10] to yield the hexaphenol **12**. The hexacatenar ethers **13** and **14** were synthesized by alkylation of the hexaphenol **12** in the usual way [11].

The pentaphenyl hexacatenars **23**–**27** were synthesized as shown in scheme 3. Compound **16** was synthesized using commercially available 1-bromo-4-iodobenzene **15** and the phenyl boronic acid **9** in a selective aryl-aryl Suzuki cross-coupling reaction in the 2-iodo-position. The trimethoxy ether **16** was demethylated in the usual way [10] to synthesize the phenol **17** followed by alkylation to synthesize the trialkoxy ethers **18**–**21** using various 1-bromoalkanes. The aryl bromides **18**–**21** were then used in cross-coupling reactions along with the commercially available 1,4-phenyldiboronic acid **22** to yield the hexacatenars **23**–**27**.

The reaction intermediates **28**–**34** were synthesized according to scheme 4 in the usual way, as shown in schemes 1–3, and then cross-coupled with the symmetrical 4,4′′-biphenyldiboronic acid **5** to synthesize the homologous series of polycatenar hexaphenyls **35**–**46** with side chains ranging from methoxy to dodecyloxy.

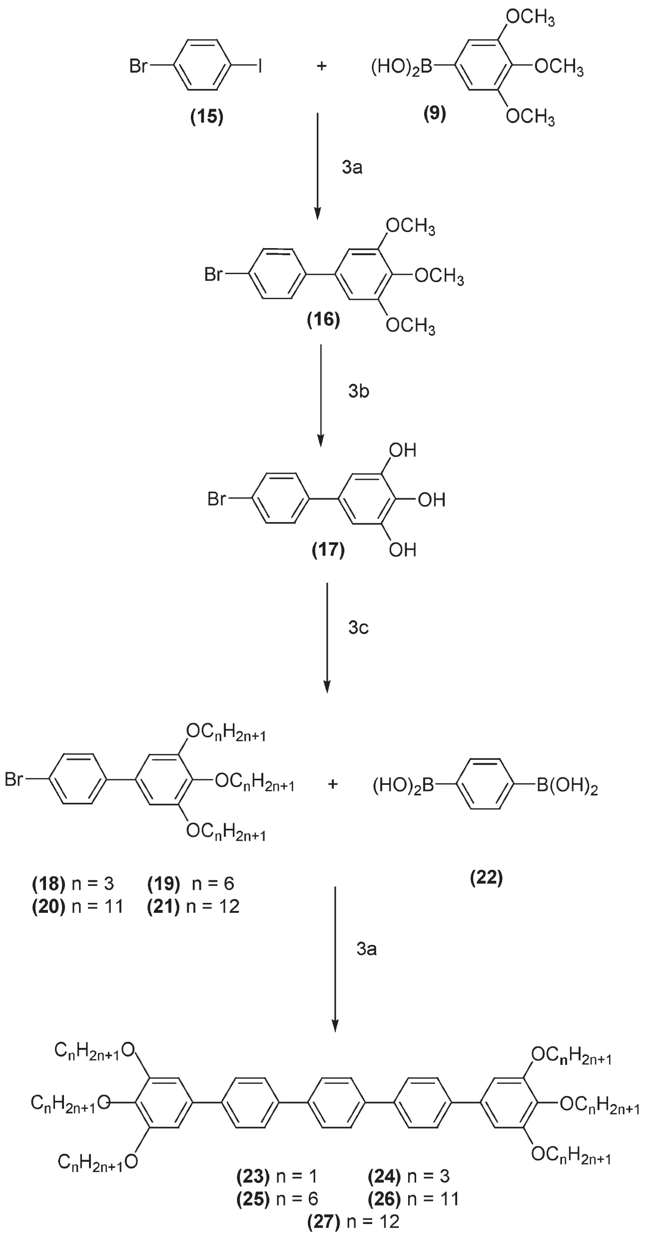
The synthesis of the 2,5-disubstituted pyrimidine **49** is shown in scheme 5. Starting material **47** is



Scheme 2. Reagents and conditions: 2a $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 2b (i) BBr_3, DCM, (iib) H_2O; 2c BrC_nH_{2n+1}, K_2CO_3, butanone.

commercially available and used along with the phenylboronic acid **9** to synthesis the aryl bromide **48**. The pyrimidine hexacatenar **49** was synthesized by the cross-coupling of compound **48** with diboronic acid **5** in the usual way.

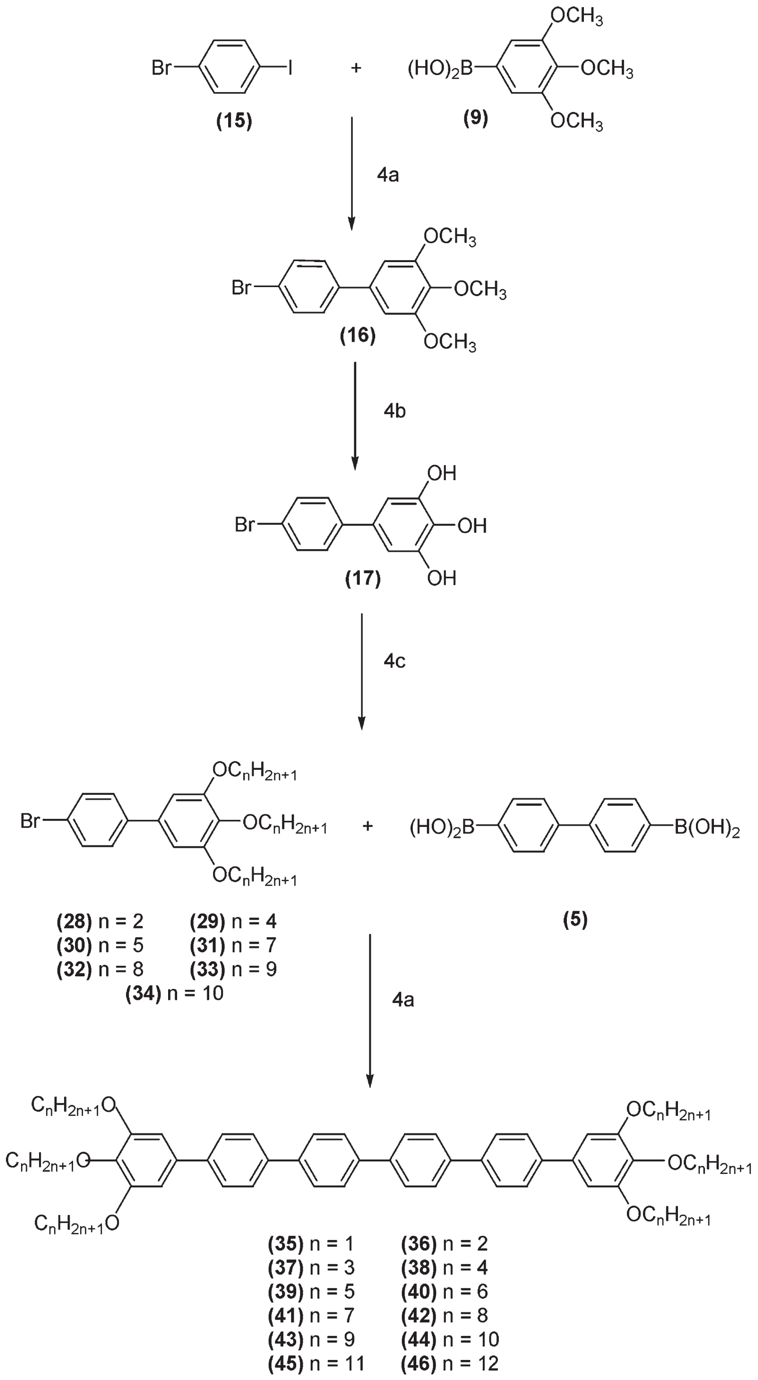
The hexacatenar pyrimidine **50** was synthesized as shown in scheme 6 using the Suzuki [12–14] aryl–aryl cross-coupling at both positions of commercially available 5-bromo-2-iodopyrimidine **47** and the phenylboronic acid **9**. The final product **52** was synthesized by *O*-alkylation using the appropriate alkyl bromide in a standard Williamson ether synthesis [11] of compound **51** prepared by demethylation of the ether **50** using boron tribromide in the usual way [10].



Scheme 3. Reagents and conditions: 3a $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 3b (i) BBr_3, DCM, (ii) H_2O; 3c BrC_nH_{2n+1}, K_2CO_3, butanone.

2.3. *Mesomorphic properties*

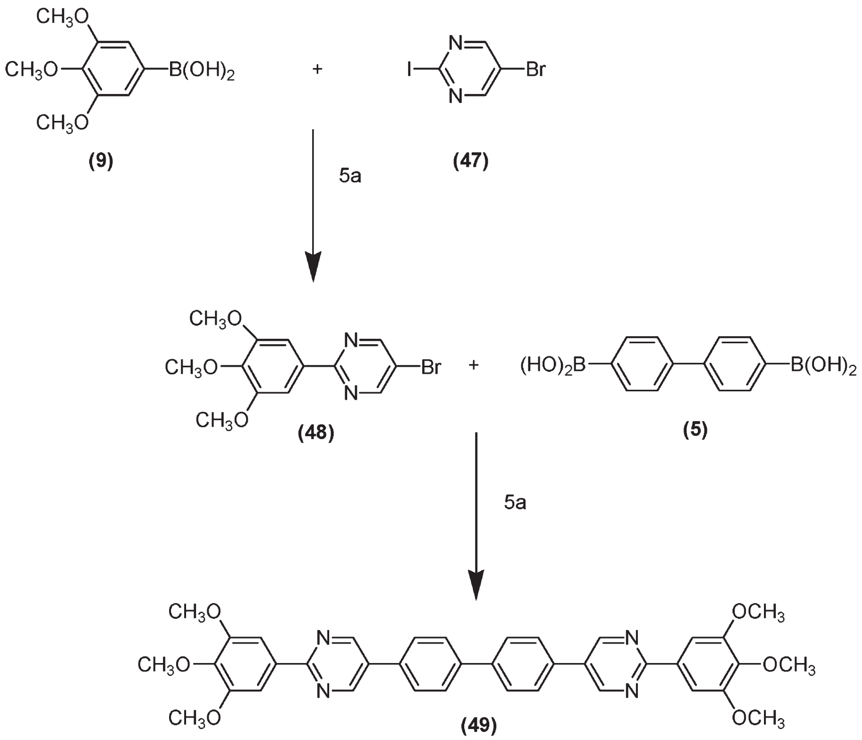
The textures of the columnar phases exhibited by most of the final compounds are varied and include the fan-like textures shown in figures 1–2. These textures are characteristic of a columnar phase. However, it is difficult to characterize the exact type of columnar mesophase exhibited by these compounds with absolute certainty without recourse to X-ray studies. The textures shown in figures 1–2 appear to indicate the presence of a hexagonal disordered columnar phase



Scheme 4. Reagents and conditions: 4a $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 4b (i) BBr_3, DCM, (ii) H_2O; 4c BrC_nH_{2n+1}, K_2CO_3, butanone.

(Col_{hd}) or a rectangular columnar phase. Homeotropic areas are observed, which is also consistent with the uniaxial nature of the hexagonal and rectangular columnar phases. Therefore, the transitions in the tables are reported as columnar phases and no distinction is made between ordered and disordered columnar phases.

The transitions observed using polarizing optical microscopy (POM) were confirmed using differential scanning calorimetry (DSC). For example, the DSC trace shown confirms the liquid crystalline transition temperatures of compound **40**. The base line of the scan is relatively flat and sharp transition peaks are observed with no thermal degradation. The clearing



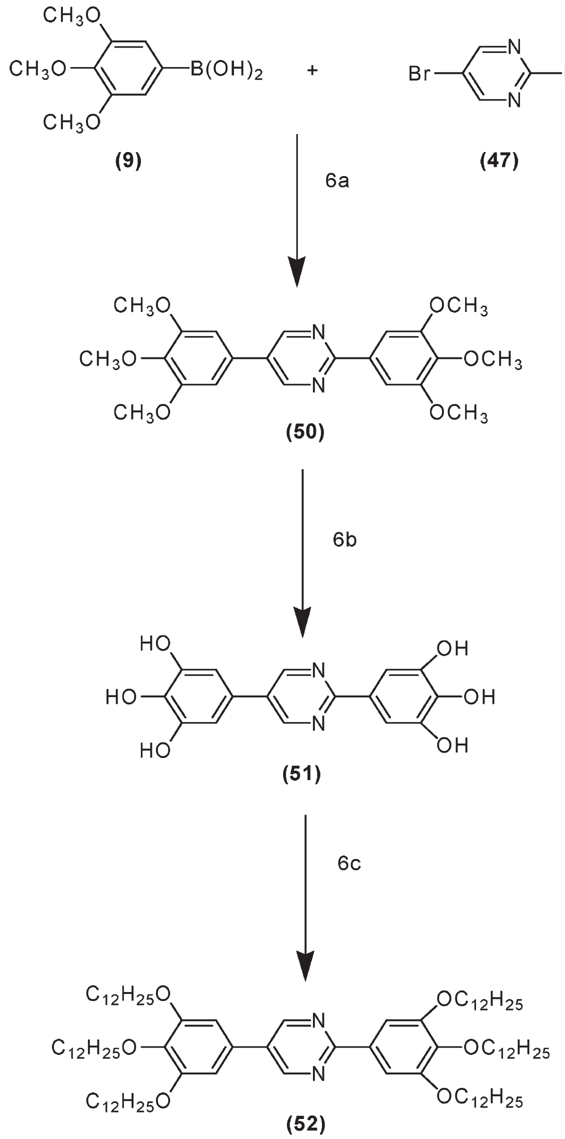
Scheme 5. Reagents and conditions: 5a $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O.

point transition is observed at 146°C with no subsequent crystallization peaks on the cooling cycles. The clearing point transition is observed in both the first and second heating cycles and is a first order transition. The transition peak, with an enthalpy ΔH=4.2 J g^{-1}, is characteristic of the transition from a hexagonal disordered columnar phases (Col_{hd}) to the completely disordered isotropic (I) liquid. The enthalpy of transition from hexagonal ordered columnar phases (Col_{ho}) would typically be much greater. The low enthalpies of fusion (0.5–6.1 J g^{-1}) of compounds **23**–**27**, for example, are also characteristic of the transition from the crystalline (Cr) state to a columnar mesophase. However, the melting of a partially crystallized state could theoretically also be responsible for a low enthalpy value for these transitions and caution should be exercised when interpreting these values.

3. Results and discussion

The phase transition temperatures and enthalpies of the tetraalkoxyquaterphenyls **6–8** (n=1, 5 and 12) are collated in table 1. The chain lengths were chosen to give a representative sample of tetracatenars with a short, an intermediate and a long chain. Compounds **6–8** exhibit a columnar phase. As the chain lengths increase so do the number of nonlinear conformations of the alkoxy chains, which results in a lowering of the melting and clearing points as the series is ascended. However, the transition temperatures of the tetracatenar compounds **6–8** are still very high. In order to produce lower transition temperatures two more terminal chains were introduced onto the same aromatic core containing four phenyl rings, to produce the hexacatenar compounds **11**, **13** and **14**. Compounds **11**, **13** and **14** contain six terminal alkoxy chains each in the 3mpm–3mpm configuration, i.e. three chains on each terminal benzene ring attached in the *meta*-, *para*-, and *meta*- positions.

The phase transition temperatures and enthalpies for compounds **11**, **13** and **14** are tabulated in table 2. Unfortunately, no liquid crystalline phase was observed with the short-chain hexacatenar compound **11** due to the high melting point and a limited amount of supercooling below the melting point. The hexacatenar compounds **13** and **14** exhibit a columnar phase due to the presence of much longer alkoxy chains and subsequent microphase separation. The presence of the two extra terminal chains in the compounds **11**, **13** and **14** results in much lower transition temperatures compared to those of the analogous tetracatenar compounds, e.g. compound **8** exhibits a clearing point of 155°C, whereas the corresponding hexacatenar compound **14** with the same chain length (n=12) has a clearing point of 45°C.



Scheme 6. Reagents and conditions: 6a $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 6b (i) BBr_3, DCM, (ii) H_2O; 6c BrC_nH_{2n+1}, K_2CO_3, butanone.

This is due to steric reasons as the additional chains lead to a broadening of the molecular rotation volume and a lowering of the effective length-to-breadth ratio. The reduction in the melting point is much greater than that of the clearing point and the melting points of the hexacatenars **13** and **14** are below room temperature.

The phase transition temperatures and enthalpies of the hexaalkoxypentaphenylenes **23–27** (n=1, 3, 6, 11 and 12) are collated in table 3. Compound **23**, which incorporates the shortest chains, does not exhibit an observable mesophase due to a very high melting point and a limited amount of super cooling below the melting point. Except for compound **23** the other homologues **24–27** with longer chains exhibit a columnar phase. This is consistent with the common observation that an increase in the chain length of polycatenar compounds favours the formation of the columnar phases to the detriment of the other phases, and that shorter chains can lead to high melting points.

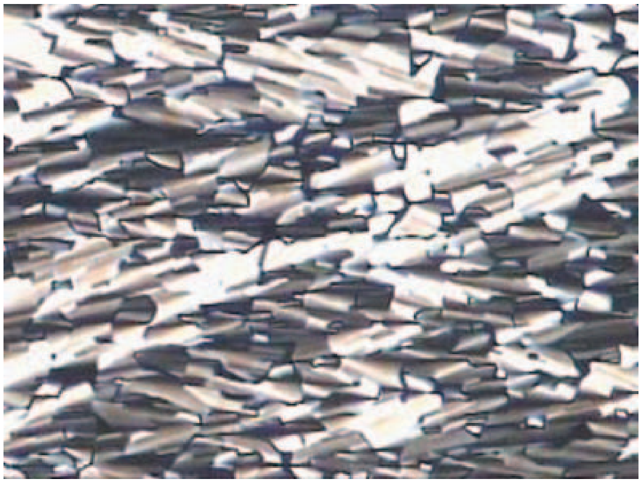


Figure 1. Photomicrograph of the fan-like texture of the columnar phase exhibited by compound **26** at 41°C as observed under POM.

The phase transition temperatures and enthalpies for the hexaalkoxyhexaphenylenes **35–46** are shown in table 4. The shorter the chain lengths of the alkoxy side chains, the higher the clearing points for the columnar phase. As the chain lengths increase so do the number of nonlinear conformations of the compounds alkoxy chains, which results in a lowering of the melting and clearing points. An odd–even pattern is observed with the decrease in the clearing points, as can be seen in figure 3. The

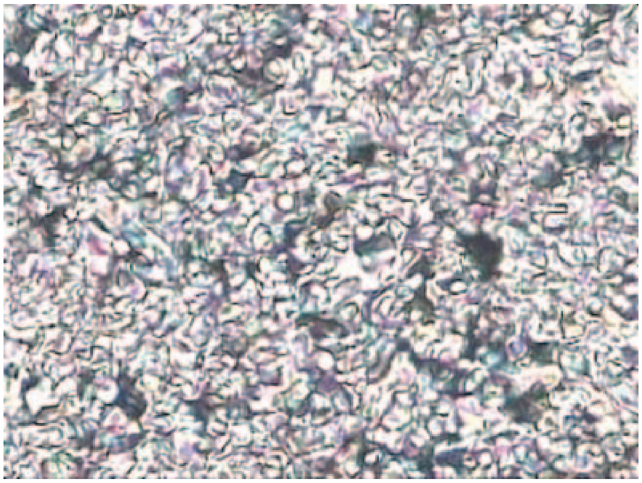
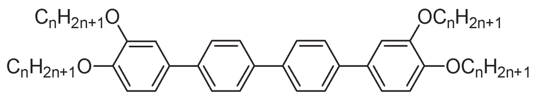


Figure 2. Photomicrograph of the mosaic texture of the columnar phase exhibited by compound **39** at RT as observed under POM.

Table 1. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the tetraalkoxyquaterphenylenes **6**–**8**.

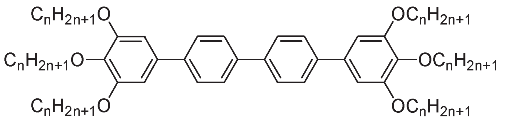


	n	Cr		Col		I
6	1	•	278 [83.5]	•	294 [9.6]	•
7	5	•	196 [13.6]	•	208 [6.1]	•
8	12	•	125 [10.5]	•	155 [4.5]	•

enthalpy of the clearing point transition also decreases rapidly on descending the series. This phenomenon may well be indicative of the higher degree of disorder attributable to the flexible alkoxy chains. Very low values are observed for long alkoxy chains. Most homologues exhibit a columnar phase at room temperature and do not crystallize above −25°C on cooling, which is also indicative of a high degree of disorder due to the chains. It may not be coincidental that the minimum in the melting point is reached for compound **46** containing the longest chains (n=12). The very high viscosity of such hexacatenars will also hinder the crystallization process and some of the materials may be metastable. Therefore, the temperature range for the columnar phase is often very broad, e.g. ranging from −50°C up to a temperature of 202°C observed for compound **38**.

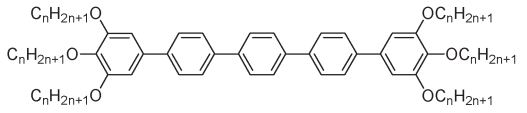
The phase transition temperatures and enthalpies of the pyrimidine hexacatenar **49** (n=1) and the *bis*-2,5-(3,4,5-trialkoxyphenyl)pyrimidines **50** and **52** (n=1 and 12) are listed in tables 5 and 6, respectively. The pyrimidines **49** and **50** with very short chains, i.e. methoxy groups, exhibit very high transition temperatures. This is probably due to a high degree of overlap of the aromatic molecular cores with very little dilution by the short alkoxy groups. The pyrimidine **50** with six methoxy chains melts at 180°C, but when the chain length is significantly increased then a dramatic reduction in the transition temperatures is observed, i.e. compound **52** with a dodecyloxy chain exhibits a columnar mesophase from below room temperature to 53°C. However, the phase transition temperatures of the pyrimidine hexacatenar **49** shown in table 5 do not differ greatly from those of the hexaphenylene compound **35** shown in table 4. The low enthalpy of fusion and the high enthalpy for the clearing point suggest that these hexacatenars containing nitrogen atoms within the aromatic rings in the central core may exhibit an hexagonal ordered, rather than a disordered, columnar phase, although this has not been confirmed by X-ray studies.

Table 2. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the hexaalkoxyquaterphenylenes **11**, **13** and **14**.



	n	Cr		Col		I
11	1	•	102 [83.5]		-	•
13	6	•	<−25		49 [7.8]	•
14	12	•	<−25	•	45 [8.8]	•

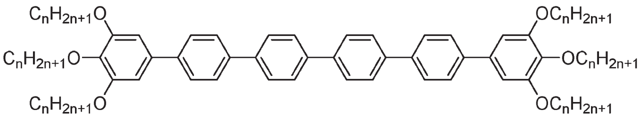
Table 3. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the hexaalkoxypentaphenylenes **23**–**27**.



	n	Cr		Col		I
23	1	•	208 [80.5]		-	•
24	3	•	178 [57.8]	•	190 [0.5]	•
25	6	•	<−50	•	107 [1.2]	•
26	11	•	80	•	106 [6.6]	•
27	12	•	34 [8.2]	•	39 [1.1]	•

The phase transition temperatures of the hexacatenar oligophenylenes **13** (m=2), **25** (m=3) and **40** (m=4), differing only in the number, m, of the 1,4-disubstituted phenyl rings attached to the phenyl rings carrying the aliphatic groups, are listed in table 7. The data collated

Table 4. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the hexaalkoxyhexaphenyls **35**–**46**.



	n	Cr		Col		I
35	1	•	209 [28.5]	•	258 [16.6]	•
36	2	•	205 [27.3]	•	231 [20.6]	•
37	3	•	203 [29.9]	•	230 [3.1]	•
38	4	•	<−50	•	202 [5.1]	•
39	5	•	<−25	•	194 [5.1]	•
40	6	•	<−50	•	163 [4.3]	•
41	7	•	<−5	•	170 [5.5]	•
42	8	•	<−25	•	148 [1.2]	•
43	9	•	<−25	•	153 [1.4]	•
44	10	•	<−25	•	133 [1.6]	•
45	11	•	<−25	•	141 [1.7]	•
46	12	•	<−25	•	110 [1.5]	•

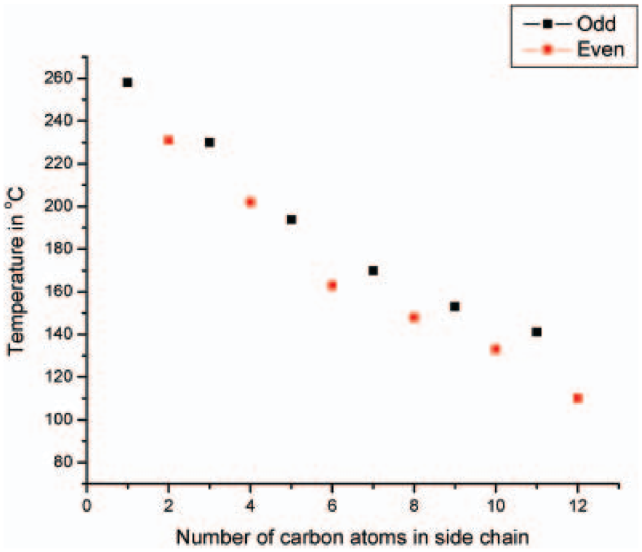
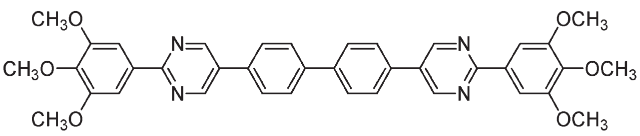


Figure 3. Graph showing the odd–even effect in the clearing point based on the number of carbons in side chains for the hexacatenar homologous series **35**–**46** (n=1–12).

in table 7 show the effect of increasing the length-to-breadth ratio of the oligomeric hexacatenars, as illustrated generally for by the oligophenylene hexacatenars **13** (m=2), **25** (m=3) and **40** (m=4). An increase in the clearing point of the columnar phase of approximately 60°C is observed for each additional the 1,4-disubstituted phenylene ring. This is due to a high degree of molecular polarizability and anisotropy of shape. The low melting point is typical of the hexacatenar compounds of these series. The fact that a columnar phase is observed for all three compounds is evidence of the direct dependence of the mesomorphism of polycatenars on the number, position and length of the alkoxy chains and neither the cores or the nature of the linkages between the cores.

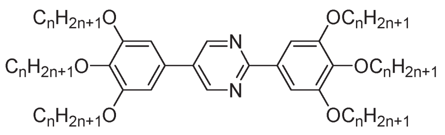
The thermal data for three hexacatenars with six dodecyloxy chains and five 1,4-disubstituted phenyl rings are recorded in table 8. The compounds differ only in the nature of the linkages between the 1,4-disubstituted phenyl rings. The symmetrical compound **53** has four unsaturated linkages [1], the unsymmetrical compound **54** three unsaturated linkages and one direct carbon-carbon bond [1], whereas the symmetrical oligophenylene **27** has only direct carbon–carbon bonds connecting the 1,4-disubstituted phenyl rings. It is evident that, although the presence of the unsaturated linkages does lead to a significantly higher degree of conjugation, a higher degree of molecular polarizability as well as anisotropy of shape, the difference in the melting and clearing points of the three hexacatenars is not great and all three compounds exhibit similar mesomorphic behaviour, i.e. columnar phases.

Table 5. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the hexaalkoxypyrimidine **49**.



	n	Cr		Col		I
49	1	•	181 [1.2]	•	250 [28.4]	•

Table 6. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in square brackets) of the *bis*-2,5-(3,4,5-trialkoxyphenyl)pyrimidines **50** and **52**.

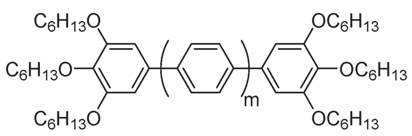


	n	Cr		Col		I
50	1	•	180 [113]		-	•
52	12	•	16 [43.4]	•	53 [43.4]	•

3.1. *Physical properties*

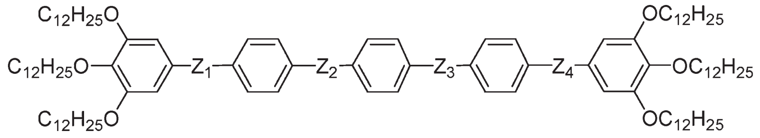
The charge carrier mobility of compound **40** was measured in the columnar phase at room temperature. A low value of $\mu_h = 5\times10^{-5}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ was measured by standard time-of-flight techniques. The majority charge carrier consists of holes due to the low ionization potential of oligophenylenes and polyphenylenes [7]. The hole mobility shows a small increase with the electric field strength (see figure 4). Charge transport in organic materials involves hopping of carriers between

Table 7. Phase transition temperatures (°C) of the oligophenylene hexacatenars **13**, **25** and **40**.



	m	Cr		Col		I
13	2	•	<−25	•	49	•
25	3	•	<−50	•	107	•
40	4	•	<−50	•	163	•

Table 8. Phase transition temperatures (°C) of the pentaphenylene hexacatenars **27**, **53** and **54** with different linkages.



	Z_1	Z_2	Z_3	Z_4	Cr		Col_1		Col_2		I
53	-COO-	-N=CH-	-CH=N-	-OOC-	•	70[a]	•	82[a]	•	92[a]	•
54	-COO-	-	-OOC-	-OOC-	•	67[a]		-	•	71[a]	•
27	-	-	-	-	•	34		-	•	39	•

[a] Literature value [1]

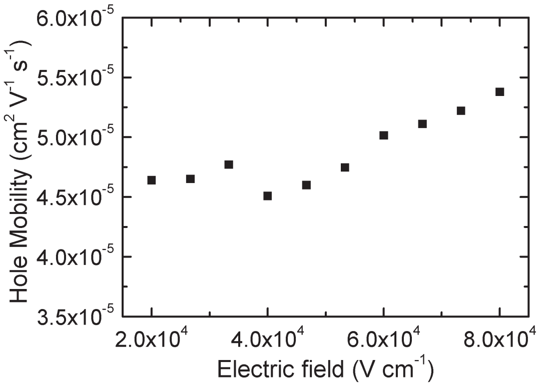


Figure 4. The hole mobility of compound **40** as a function of applied electric field.

the aromatic cores of molecules and so requires a high overlap between their π-conjugated systems. This occurs in discotic triphenylenes and porphyrins, where the molecular cores are aligned along the columns thus showing high mobility values. The low mobility observed here implies a poor overlap between the cores of the molecules in adjacent layers of the columns as well as a poorer overlap between molecules in different columns.

4. Conclusions

The absence of conjugated linkages between the aromatic rings in the cores of polycatenars does not affect their mesomorphic behaviour significantly and aryl–aryl cross-coupling reactions are an attractive route to polycatenars. The number of 1,4-disubstituted phenyl rings in the core of the molecule determines the magnitude of the liquid crystalline transition temperatures, but not the type of mesophase formed. This appears to be solely dependent upon the number, length and position of the aliphatic chains. The presence of nitrogen atoms in the aromatic rings in the cores of the molecules does not affect the liquid crystal behaviour significantly. The combination of oligophenylenes and six long alkoxy chains leads to low melting points and very wide temperature ranges for columnar phases. The charge carrier mobility of columnar phase of polycatenar compounds is low due to the poor overlap of the π-electron density within the columns and the high concentration of aliphatic chains.

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