PERKIN 2

Synthesis, phase behaviour and polymerisation of mesogenic materials based on 3-substituted pyrroles

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Synthetic routes which lead to the formation of 3-substituted pyrroles with mesogenic units are described. Two particular compounds have been prepared: 3-{6-[4-(4-methoxyphenylazo)phenoxy]hexyl}pyrrole and 3-[6-(4′-cyanobiphenyl-4-yloxy)hexyl]pyrrole. Both exhibit monotropic liquid crystalline phases, and for the latter compound the stability of the mesophase observed could be increased by incorporation of a small amount of a commercially available liquid crystal. Electrochemical investigations show that the azobenzene based material is a poor candidate for the formation of polypyrrole derivatives, because of the ease with which competing oxidative processes occur. The cyanobiphenyl derivative, in contrast, has been polymerised electrochemically to form electrically conducting polymer films; these films reveal an electrochromic effect by virtue of reversible doping. It has also proved possible to polymerise this material chemically to give a polymeric material which is soluble in a variety of solvents. A further procedure involved oxidation with bromine vapour to polymerise the material in an aligned state; the yields of such polymers, however, are poor, and considerably lower than those obtained for materials prepared in the isotropic melt.

Introduction

A wide range of polymeric materials can act as electrically conducting polymers; the common feature of such materials is extended conjugation of the polymer backbone. As such, the simplest conducting polymer is polyacetylene.[1,2] This material can be prepared with conductivities as high as 10^5 S cm^{-1}; however, it is extremely unstable to both air and moisture, severely restricting its practical utility. Polypyrrole, (and related materials such as polyaniline and polythiophene) in contrast, can be readily prepared through either the chemical[3] or electrochemical[4] oxidation of the appropriate monomer to give flexible, free-standing films which are stable in air. Although through careful control of the growth conditions, anisotropic films can be prepared,[5] these are essentially highly disordered materials.

One major problem with polypyrrole, and with many conducting polymers in general, is their intrinsic inability to be processed. This arises from the necessarily rigid nature of the polymer backbone. A number of routes to increasing the melt processibility and/or solubility have been tried, but perhaps the most simple and important one is the preparation of derivatives of the monomer which bear flexible side-chains, prior to polymerisation. This approach has been found to be particularly applicable to the heterocycles, pyrrole and thiophene. For pyrrole such derivatives may include *N*-methylpyrrole,[6] higher *N*-alkylpyrroles[7] and materials substituted at one or both the 3-positions in the pyrrole ring.[8] Substituted pyrroles[9] and related thiophenes[10] have been found to be soluble in a range of solvents depending on the nature of the substituent, although in general it is rather more difficult to produce materials which are soluble in the doped (conducting) state than in the undoped (insulating) state.[11]

The development of processible conducting polymers has prompted investigations into systems with the potential for forming a mesophase, either in the precursor monomer, or in the polymer itself. Such materials are of particular interest because there is potential for enhanced orientation with a possible improvement in the properties of the materials.[12] Thus mesogenic materials based on thiophene,[13,14] pyrrole (substituted in both the 3-position[15–17] and at the nitrogen[18–20]) and more recently aniline,[21] have been prepared. In this contribution we extend our preliminary investigations in this area[15] and describe some general methods for the preparation of pyrrole derivatives, factors which influence mesophase formation of such materials, and their oxidation both chemically and electrochemically to form poly(3-substituted pyrroles).

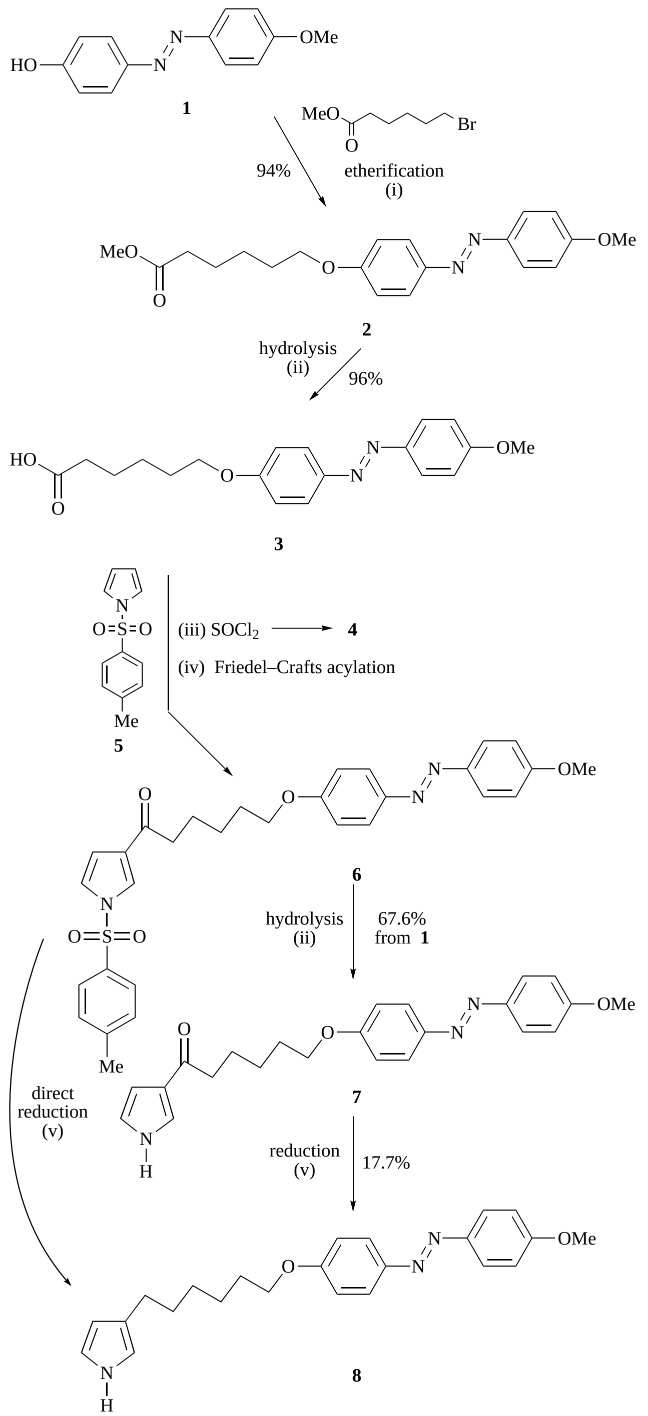
Results and discussion

Synthesis

In the investigations described here we have focused on the preparation of pyrroles with rigid aromatic units (the mesogen) attached at the 3-position *via* a methylene chain. We have designed two synthetic pathways to produce molecules of this type, both reliant on the directing effect of an aryl sulfonated group attached to the *N*-position of the pyrrole ring, to effect 3-substitution.[22,23]

The first method for the preparation of potentially mesogenic pyrrole is outlined in Scheme 1 (steps i–iv) for 3-{6-[4-(4-methoxyphenylazo)phenoxy]hexyl}pyrrole (**8**). Specific problems with the route outlined were, firstly, the reduction step, which required careful selection of reagents to avoid adventitious polymerisation of the product; ultimately, sodium borohydride in refluxing propan-2-ol was selected;[24] secondly, the difficulty in obtaining selective attack at the 3-position of the pyrrole ring. A range of conditions were investigated for the coupling between 6-[4-(4-methoxyphenylazo)phenoxy]hexanoyl chloride (**4**) and *N*-tosylpyrrole (**5**), as illustrated in Table 1. It would appear that the regiospecificity is independent of the concentration of **5** and the reaction temperature but that the formation of the 3-substituted product is favoured by performing the reaction in dilute homogeneous solution; in contrast, a more concentrated solution of the complex favoured substitution at the 2-position. A quantity of the 2-derivative formed during these investigations was carried forward to give the 2-substituted alkylpyrrole (**8α**), in order that its phase behaviour could be examined and compared to the 3-derivative.

The problems encountered in acylating pyrrole in the 3-position prompted us to investigate general routes by which a common intermediate could be used to prepare a range of potentially mesogenic materials. We focused on *N*-(benzene or toluene-*p*-)sulfonyl-3-(6-bromohexanoyl)pyrrole [(**9**) and (**9A**),



Scheme 1 Complete synthetic pathway to 3-{6-[4-(4-methoxyphenylazo)phenoxy]hexyl}pyrrole (**8**). *Reagents and conditions*: (i) K_2CO_3, DMF, 90 °C; (ii) 1,4-dioxan, 5 M aq. NaOH, room temp. or reflux; (iii) $SOCl_2$, DMF (trace); (iv) $AlCl_3$, CH_2Cl_2, room temp. then H_2O; (v) $NaBH_4$, propan-2-ol, reflux 24–48 h.

respectively] as common intermediates (Scheme 2). These materials were prepared in high yield from the acylation of the corresponding *N*-arenesulfonylpyrrole (**5**) or (**5A**) with 6-bromohexanoyl chloride. Scheme 2 shows possible routes for the synthesis of **8** and 3-[6-(4′-cyanobiphenyl-4-yloxy)hexyl]-pyrrole (**12**), although the methodology should apply equally well to other mesogenic units (but see below). Unfortunately, the more direct of these two routes (Scheme 2, step iii) gave rise to a number of products; *e.g.* when **1** was reacted with **9** directly the desired compound **6** was formed, together with 4-(4-methoxyphenylazo)phenyl toluene-*p*-sulfonate (**13**) and substantial quantities of the hydrolysis product **7**. In spite of this problem, a considerable advantage to this approach is that the reduction and hydrolysis of **6** can be performed concomitantly, using sodium borohydride in refluxing propan-2-ol (Scheme 2, step iv). In general, however, it was considered more appropriate to proceed *via* the hydrolysed 3-acylpyrrole (**10**), in order to minimise the formation of hydrolysis products. This methodology was applied to the reaction of **10** with other rigid-rod type phenols, namely 4-cyanophenyl 4′-hydroxybenzoate (not shown) and 4′-cyano-4-hydroxybiphenyl (shown in Scheme 2). In the former case, a Williamson ether synthesis yielded only 4-cyanophenyl 4-[5-(pyrrol-l-yl carbonyl)-*n*-pentyloxy]benzoate], indicating that even the very weakly basic conditions of the ether synthesis were sufficient to hydrolyse the aromatic ester. For the latter, however, the reaction could be carried through to the desired 3-[6-(4′-cyanobiphenyl-4-yloxy)hexyl]pyrrole (**12**) in reasonable yield (Scheme 2, steps iii–iv), the main losses appearing to arise from substantial polymerisation in the reduction step.

To summarise the synthetic methodologies available, the reader is therefore left to choose between: (*i*) formation of derivatives of the type exemplified by **6**, either by the rather tedious route outlined in Scheme 1, or from the reaction of the common derivative **9** with the appropriate phenol (Scheme 2), necessitating the separation of a mixture of products; both strategies yield **6**-type derivatives which undergo clean and efficient reduction to the desired 3-alkylpyrrole derivative; or (*ii*) reaction of the phenol derivative with the cleanly prehydrolysed derivative **10**, to furnish derivatives typified by **7** and **11**, but which undergo reduction in rather poor yields.

Phase behaviour

The phase behaviour of the two 3-substituted pyrroles observed by optical microscopy are listed in Table 2. Disappointingly, only monotropic liquid crystalline phases could be observed for both these materials. The optical texture suggested that in both cases a nematic phase was formed. The nematic phase for the azobenzene derivative **8** was found to persist over a greater temperature range than that for the cyanobiphenyl derivative **12**, with the former being observed over a 30–35 °C temperature range, whilst the latter existed over only about 15 °C range and was particularly prone to spontaneous crystallisation. The DSC traces obtained on cooling from the isotropic melt for these samples are shown in Fig. 1.

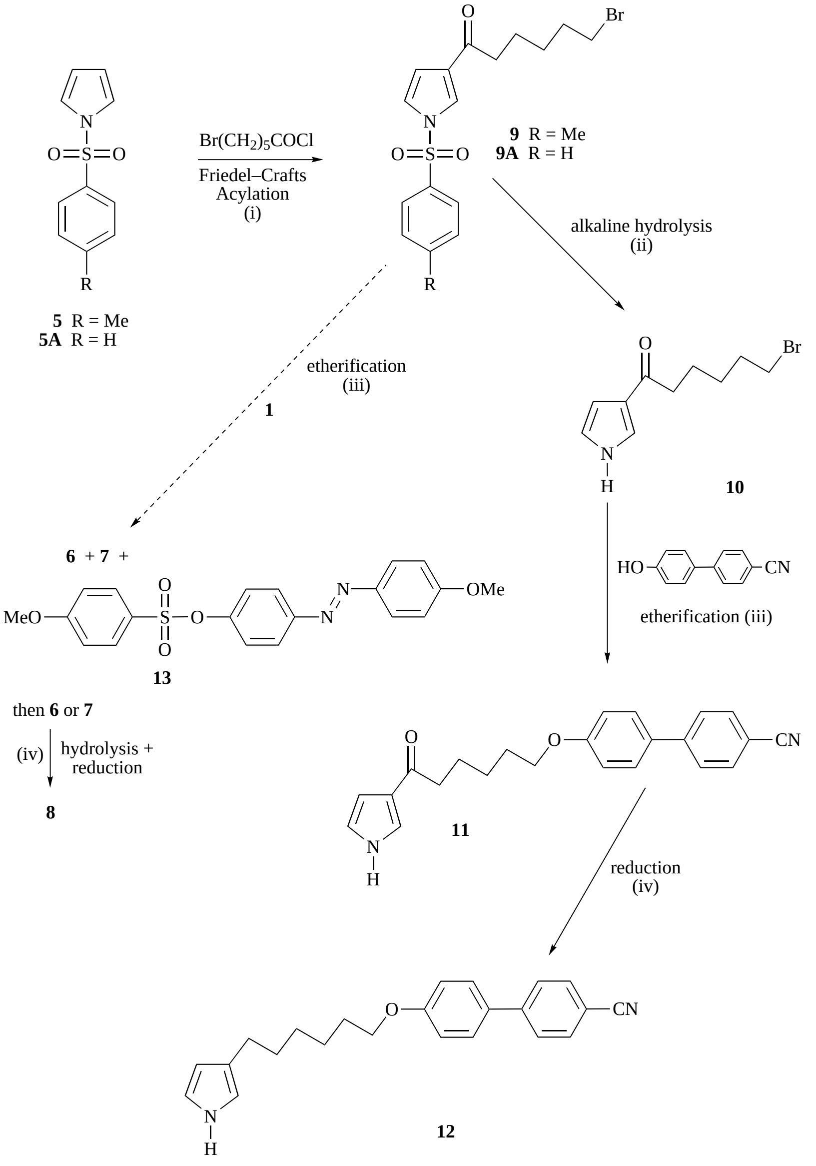
In order to evaluate the factors which might influence mesophase formation in these pyrrole derivatives, the phase behaviour of a range of derivatives of 4-methoxy-4′hydroxyazobenzene **1** was investigated, specifically to determine the influence, if any, of hydrogen bonding. The data obtained from such materials are listed in Table 3. It can be seen that with the exception of the carboxylic acid derivative **3** (where dimerisation preserves the linearity of the molecule and increases the molecular length in line with other carboxylic acid derivatives),[25] only the alkyl-terminated material gives a stable mesophase; in other examples monotropic phases were observed or in some cases, where crystallisation was a relatively slow process, the nematic structure was apparent where crystallisation had not occurred on cooling. Thus, the presence of dipolar or hydrogen-bonding interactions clearly inhibits mesophase formation, although this may be, to some extent, offset when conjugation increases the polarisibility of the molecule (*cf.* the phenyl derivative **15**), and presumably it is this effect which allows the formation of an (albeit monotropic) mesophase for the 3-substituted pyrroles described here.

In view of the desirability of stable mesophases in relation to polymerisation studies mixtures of the cyanobiphenyl derivative **12** and the commercial liquid crystal 4-cyano-4′(*n*-hexyloxy)biphenyl (M18; Merck Ltd) were prepared. A range of thermoptic cooling curves obtained for mixtures of M18 and **12** are shown in Fig. 2. It is apparent from these studies that, first, these mixtures underwent an isotropic liquid crystal transition at temperatures in the region 70–76 °C (the observed

Table 1 Regiospecificity of the Friedel–Craft's acylation of *N*-tosylpyrrole (NTP) (**5**) with 6-[4-(4-methoxyphenylazo)phenoxy]hexanoyl chloride (**4**) and $AlCl_3$ in CH_2Cl_2

Reaction step	$[RCO^+AlCl_4^-]$[a,b]/mmol ml^{-1}	[NTP]/mmol ml^{-1}	*T*/°C	Isomer formed[c]
i	0.21	0.26[d]	0	2-
ii	0.06	0.14	−5	3-
iii	0.22	0.49	−5	2-
iv	0.09	0.68	20	3-
v	0.26[e]	0.68	20	2- and 3-

[a] Molarities given are not true molarities; rather, they reflect the number of mmoles of reagent present for each ml of solvent added. [b] Estimated from the number of moles of the limiting reagent (RCOCl) added to form a 1 : 1 complex with $AlCl_3$. [c] Identified from ^1H NMR spectroscopy of the subsequently hydrolysed product. [d] *N*-(Benzenesulfonyl)pyrrole) was used. [e] The acid chloride added was not homogeneous.



Scheme 2 General synthetic route to mesogenic 3-substituted pyrroles: method 2. *Reagents and conditions*: (i) AlC_3, CH_2Cl_2, room temp. then H_2O; (ii) 1,4-dioxan, 5 M NaOH, room temp. or reflux 24 h; (iii) K_2CO_3, KI (trace), DMF, 70–90 °C; (iv) $NaBH_4$, propan-2-ol, reflux 24–48 h.

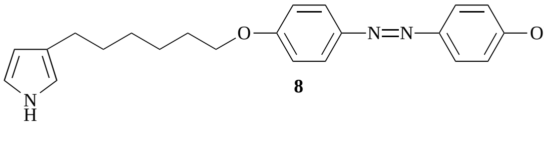
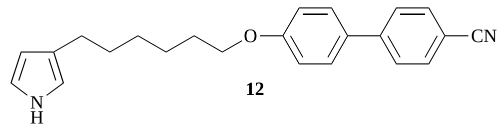
optic texture was consistent with a nematic phase); secondly, on increasing the proportion of M18, there is an initial decrease in T_{NI} followed by fairly gradual increase to the value of the pure liquid crystal; thirdly, the onset of crystallisation in both pure compounds is sharp and above 40 °C, but on mixing the two compounds, the onset of crystallisation is shifted to lower temperatures and occurs at a much lower rate than for either pure compound.

The above discussion illustrates, that while the formation of a monotropic phase for both **8** and **12** was disappointing, both materials could potentially be used in experiments in which the polymerisation is performed in the liquid crystalline phase: the former by virtue of the broad temperature range over which a monotropic phase is observed; the latter by using mixtures with the commercially available liquid crystal M18.

Polymerisation of 3-substituted pyrroles

Cyclic voltammetry studies. Fig. 3(*a*) shows the traces obtained from successive cyclic voltammetry (CV) scans of the cyanobiphenyl derivative **12**. Features appear at potentials (*vs.* SCE) of 1.22 and 1.75 V, together with a shoulder on the latter peak at 1.57 V. Similarly, the azobenzene derivative **8** exhibited overlapping peaks at 0.91, 1.16 and 1.35 V; these values compare with 1.24 and 1.50 V for pyrrole under similar conditions.

Table 2 Thermo-optical analysis of the 3-substituted pyrroles bearing terminal mesogenic groups

	Phase transition/°C[a]		
3-Substituted pyrrole	C←N	N→I	C→I
 **8**	(52.3)[b]	(77.3)	98.6
 **12**	(68.7)[b]	(72.4)	C_1 86.0 C_2 96.6

[a] Parentheses indicate a monotropic transition. [b] Temperature at which recrystallisation is observed to occur.

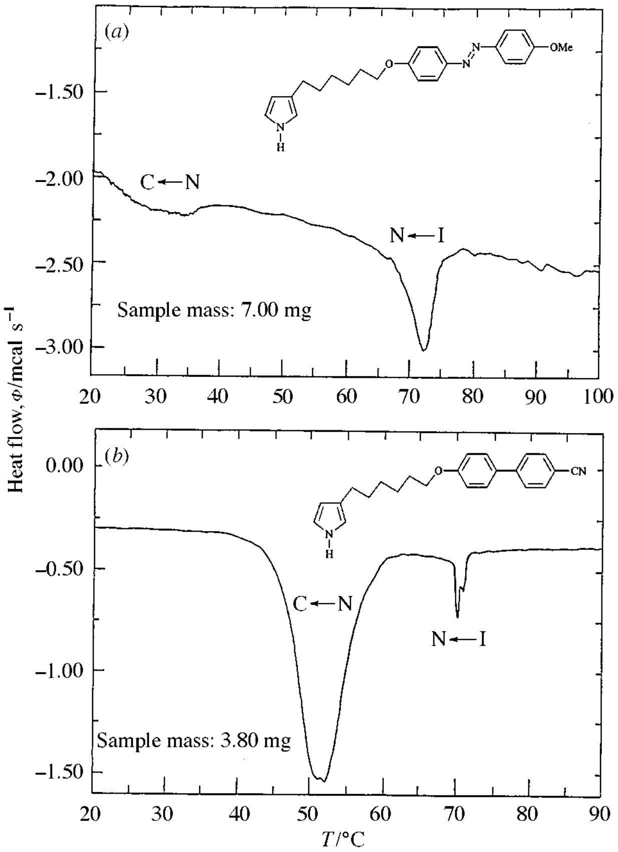


Fig. 1 Differential scanning traces obtained from the 3-substituted pyrrole derivatives prepared here; the traces were obtained on cooling from the isotropic melt at a cooling rate of 10 °C min^{-1}. Curve (*a*) shows the trace obtained from **8**; curve (*b*) shows the trace obtained from **12**. In both cases the heating traces showed only a crystalline–isotropic transition.

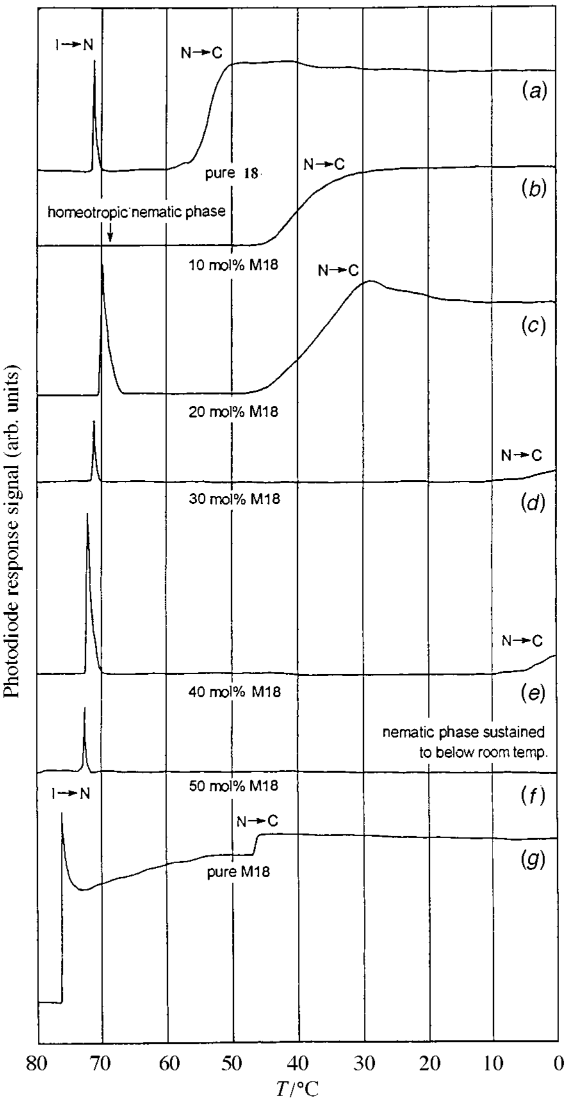


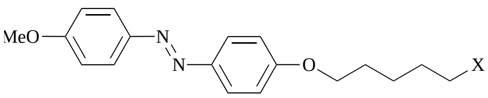
Fig. 2 Range of thermoptic cooling curves obtained for mixtures of M18 and **12**; addition of M18 in increasing quantities diminishes the onset of crystallisation to lower temperatures (curves *b*–*f*) and this occurs at much lower rates than for either compound alone

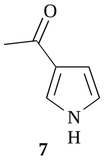
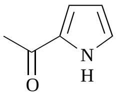
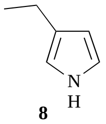
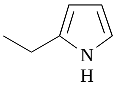
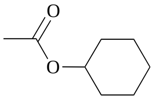
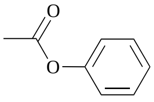
The different peak potentials at the more anodic voltages for the 3-substituted pyrroles suggests that these arise from different chemical processes, *i.e.* by decomposition of the aromatic side-groups. Restricting the scan to a voltage just past the first oxidation peak gave the curve shown in Fig. 3(*b*) for the monomer **12**. Under these conditions a polymer film was deposited on the electrode. The colour of this film was found to vary with potential, and continued cycling permitted thicker films to be formed.

Polymer films could not be formed for the azobenzene derivatives, even when switched near the onset of the earliest peak at *ca.* 1.2 V. Under these conditions, there was a gradual increase in current with successive scans suggestive of limited polymerisation. In addition a reddish suspension was formed at the anode; this appeared to stream away and dissolve in the bulk solution. This is presumably due to the formation of soluble oligomeric products, such as those observed from 3-alkylthiophenes.[26]

Thin films of poly{3-[6-(4′-cyanophenyl-4-yloxy)hexyl]pyrrole} [poly(12)]. Thin films of poly(**12**) were analysed to evaluate the effect of the dopant on their behaviour. These films

Table 3 Phase behaviour of 4-methoxy-4′-(terminally substituted)hexyloxyazobenzenes



X	Heating/°C[a]			Cooling/°C[a]		
	C→N	N→I	C→I	I→N	N→C	I→C
-CH_3[b]	40	51	—	51	na	—
-COOMe **2**	—	—	104.7[c,d]	74.6[c,e]	—	100.7[c]
-COOH **3**	153.9	160.0	—	156.5	150.4	—
 **7**	—	—	150.2[c]	—	—	131.2[f]
 **7a**	—	—	126.2[c,d]	82.4[g]	—	109.1[c]
 **8**	—	—	98.6[c,d]	77.3–75.0	52.3[c]	—
 **8a**	—	—	110.7[d]	52.3–48.7[c]	44.2[c]	—
 **14**	—	—	84.3	48.9–48.7	—	68.8
 **15**	—	—	100.2[c,d] 110.6[h]	98.6–96.9	87.8	—

[a] Heating/cooling rate of 1 °C min^{-1}, unless otherwise stated. [b] Values taken from ref. 35. [c] Heating/cooling rate of 2 °C min^{-1}. [d] Some crystal structure rearrangement takes place prior to the clearing point indicated. [e] Transient nematic phase observed as isolated droplets or by supercooling isotropic melt. [f] Cooling rate of 10 °C min^{-1}. [g] Cooling rate of 5 °C min^{-1}. [h] A different and more thermally stable crystal structure grew out of initial isotropic melt to give a second, higher clearing point.

were prepared on a platinum bead electrode from a solution of the monomer in acetonitrile containing tetraethylammonium tetrafluoroborate (0.1 M). The polymer-coated electrode was then placed in a fresh solution of tetraethylammonium tetrafluoroborate and driven between the reduced and oxidised states. It was found that the electrochemical cycle could be driven repeatedly with little change in the peak currents being observed. Fig. 4 shows cyclic voltammograms obtained at various scan rates for a sample of poly(**12**) in acetonitrile containing tetraethylammonium tetrafluoroborate. Neither the oxidation nor the reduction wave have the shape expected for a diffusion controlled process, and the curves rather represent the behaviour of an electroactive coating that alters its condition morphology and composition during the scan.[27] A linear relationship was found to exist between the peak current and scan rate; this is generally indicative of an electroactive process that is localised to the electrode surface. Similar electrochemical behaviour was observed when BF_4^- was replaced with PF_6^- as the dopant, although a shift in the voltage at which oxidation occurs was observed. In contrast, both bromide and toluene-*p*-sulfonate give poorly defined CV traces (*i.e.* little current was passed on cycling). In the latter case, it seems likely that this large counter-ion cannot diffuse through the pores in the polymer matrix, in agreement with the extensive observations of Walton *et al.*[27] The result obtained for the relatively small bromine ion is somewhat anomalous, but this may be due to chemical reaction of the nucleophilic bromine ions with the oxidised polymer backbone to form covalent C–Br bonds.

As for polypyrrole, the reversible doping of the counter-ion is accompanied by an electrochromic change and the colours observed at various points on the sweep are indicated in Fig. 4. The UV–VIS spectrum of the reduced form showed a strong absorption below 350 nm, together with a shoulder at 375 nm, and a relatively weak broad peak at 500 nm. For the oxidised form a strong absorption at 350 nm was also observed, together with rather broad absorptions at 950 and 700 nm. This behaviour qualitatively resembles that observed for polypyrrole.[28]

Chemical polymerisation. Monomer **12** could by polymerised chemically in acetonitrile solution using copper(II) perchlorate (see Experimental section).[29] The resultant polymer was

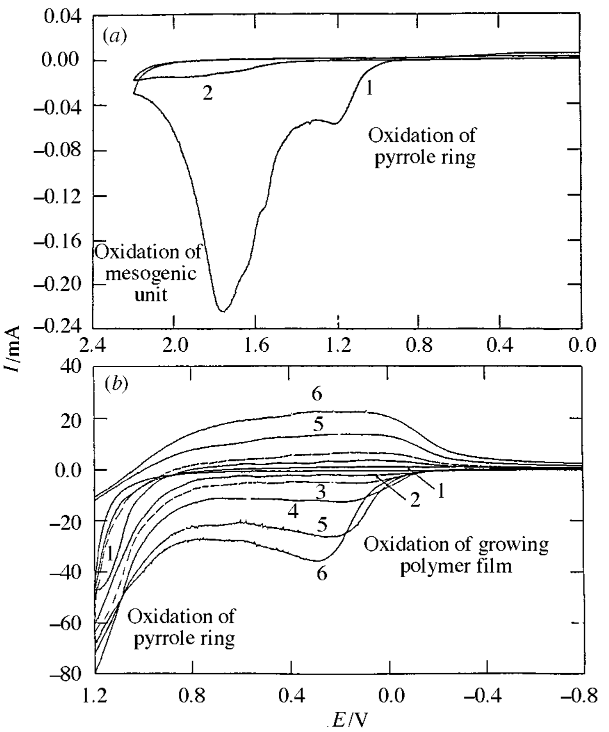


Fig. 3 Cyclic voltammetry curves (numbered chronologically) for the oxidation of **12** (*ca.* 1×10^{-3} mole dm^{-3}) in acetonitrile containing tetraethylammonium tetrafluoroborate (0.1 mol dm^{-3}) as the background electrolyte (potential measured relative to SCE); (*a*) shows the curve obtained on cycling to 2.2 V *vs.* SCE; apparently the side-group is oxidised; (*b*) illustrates the curve obtained with a switching potential of 1.2 V *vs.* SCE

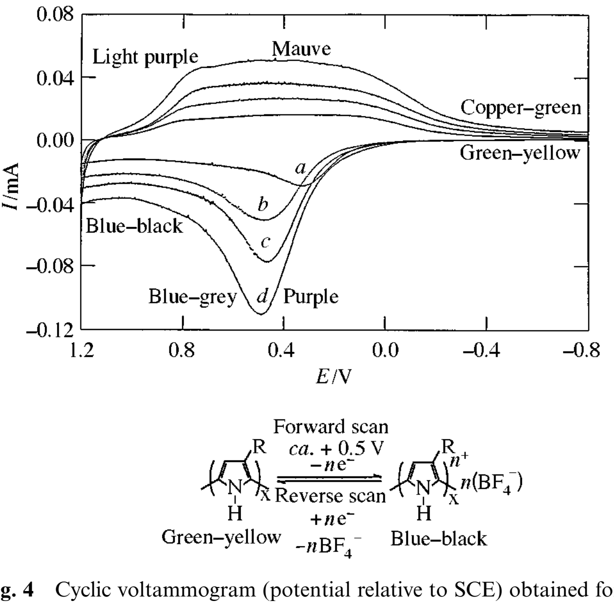


Fig. 4 Cyclic voltammogram (potential relative to SCE) obtained for poly(**12**) at different scan rates. (*a*) 30 mV s^{-1}, (*b*) 50 mV s^{-1}, (*c*) 70 mV s^{-1}, (*d*) 100 mV s^{-1}. The colour of the electrode surface is indicated at appropriate points on the curve.

obtained as a black solid. Elemental analysis gave C: 72.64; H: 5.71; N: 7.53; Cl: 0.37%, which, assuming the 'missing' mass to be due to incombustible material, gives an empirical formula of $C_{23}H_{21.1}N_2(ClO_4)_{0.039}$. This value is broadly in agreement with the expected value of $C_{23}H_{22}N_2(ClO_4)_n$ and clearly indicates a low level of doping; in contrast, polypyrrole prepared under identical conditions gave an empirical formula of $C_{4.01}H_{3.22}N(ClO_4)_{0.30}$, *i.e.* the level of doping was found to be an order of magnitude higher.

The polymer obtained from the cyanobiphenyl derivative **12** was found to be slightly soluble in a number of solvents; typically, for the better solvents such as DMA (*N*,*N*′-dimethylacetamide), about 1 mg of polymer dissolved in 100 ml of solvent. The UV–VIS spectra obtained for the polymer in DMF (dimethylformamide) showed two broad bands centred at 724 and 393 nm and IR spectra of the material showed no evidence of the tail of the 1 eV band characteristic of doped polypyrrole,[8] once again confirming the relatively low level of doping in this material. No evidence of melting or any other phase behaviour was obtained for this polymer.

Oxidation of the cyanobiphenyl derivative **12**, was performed under anaerobic conditions using ferric chloride as the oxidant. A portion of the black solid obtained was dissolved in DMF to give an intensely blue–black solution. The UV–VIS spectrum of this solution revealed only a broad, rather featureless absorption between 1100 and 400 nm. No change in the electronic spectrum could be observed when either oxygen or bromine vapour were bubbled through the solution, suggesting that the material is not readily doped (the IR spectrum of this material was similar to that obtained from the polymer prepared using copper perchlorate).

Thin films of poly (**12**) could be prepared by evaporation (at reduced pressure and elevated temperature) of the solvent from a saturated polymer solution cast on to a glass slide. The grey–black polymer film obtained was rather patchy in appearance and showed only a gradual increase in absorbance from 800 nm into the ultraviolet in its UV–VIS spectrum. No apparent phase behaviour was observed from this film on heating to 280 °C.

Polymerisation of the aligned monomer 12. In order to investigate the possibility of forming samples of poly (**12**) with a degree of global alignment, the monomer was polymerised in a specially constructed cell[18] by exposure to bromine vapour. It was generally found that the nature of the film formed varied with the conditions employed. Samples of monomer, either aligned macroscopically (on a rubbed polyimide slide) or in the isotropic melt (at *ca.* 80 °C), yielded thin, black, brittle films on exposure to bromine vapour. Unfortunately, unreacted monomer was found to be trapped beneath the flexible polymer 'skin'; thicker samples of 'polymer' could be obtained by prolonging the reaction time. One such sample (prepared from polymerising the monomer in its 'aligned' nematic state at *ca.* 60 °C) was carefully peeled off the glass surface and mounted in the beam of an X-ray diffractometer containing a photographic plate. The resultant X-ray photograph contained many sharp, circular rings (the inner ring corresponded to a spacing of 7.6 Å), interspersed with points. This is clearly indicative of a highly crystalline solid and again confirms that polymerisation had only occurred on the surface of the sample. The quality of the film morphologies also appeared to be dependent on the reaction conditions. It was found that much smoother, coherent (but brittle) films were obtained by polymerising the isotropic melt rather than the anisotropic mesophase. This implies a much more efficient polymerisation process in the isotropic phase, in line with the observations of Vicentini *et al.*[17]

Conclusions

3-(6-Bromohexanoyl)pyrrole (**10**) provides a powerful starting point for the preparation of a range of potentially mesogenic pyrrole based systems. Some simple derivatives prepared here showed only monotropic liquid crystal phases, and it would seem likely that stable mesophases would be best achieved by increasing the length of the mesogenic portion of the molecule (by, for example, including an additional aromatic ring); the stability of the liquid crystal phase, however, can be increased by incorporation of a small quantity of thermotropic liquid crystal. The material prepared here could be polymerised both chemically and electrochemically, although the two chemical methods utilised yielded materials which contained, at best, only very light levels of doping. Polymerisation of the cyanobiphenyl-based system (**12**) in an aligned state gave poor yields of poly (**12**), the polymerisation being considerably more efficient in the unaligned isotropic state.

Experimental

Methods

Elemental analysis was performed by Medac Ltd., at the Chemistry Department, University of Brunel. High resolution NMR † spectra were recorded in $CDCl_3$ (unless otherwise stated) on either a Bruker WM250 (250 MHz) or a JOEL JNM-EX400 (400 MHz) Fourier Transform Spectrometer. All coupling constants J are measured in Hz. Low resolution EI and CI (NH_3) mass spectra were obtained from the EPSRC Mass Spectrometry Service Centre, University College of Wales, Swansea. Accurate masses were obtained at Reading using a V.G. Micromass 7070F mass spectrometer, with an accelerating potential of 70 eV.

The apparatus for phase transition measurements using optical microscopy and DSC are described elsewhere.[30] Cyclic voltammetry was performed using an EG & G Princeton Applied Research Versastat® potentiostat, running their Model 250 Electrochemical Analysis System software. All potentials were measured relative to the saturated calomel electrode (*vs.* SCE) ($E°$ 0.248 V at 20 °C).

Materials

All solvents and reagents were commercially available and used as supplied except acetonitrile, dichloromethane, pyrrole and tetrahydrofuran, which were purified using procedures adapted from Perrin and Armarego.[31] *N*-(Toluene-*p*-sulfonyl)pyrrole (**5**) and *N*-benzenesulfonylpyrrole (**5A**) were prepared by the reaction of potassium pyrrole and the appropriate sulfonyl chloride, according to the literature method.[32] 4-Cyanophenyl 4′-hydroxybenzoate was prepared *via* esterification of 4-cyanophenyl with 4-acetoxybenzoyl chloride, according to the method of Sempuku.[33] Cyclohexyl 6-[4-(4-methyoxyphenylazo)phenoxy]hexanoate (**14**) was prepared from **3** using the general procedure of Neises and Steglich,[34] and phenyl 6-[4-(4-methoxyphenylazo)phenoxy]hexanoate (**15**) was prepared by the reaction of the acid chloride (**4**) with phenol. The procedures used for the preparation of the other materials described in this account are given below.

Methyl 6-[4-(4-Methoxyphenylazo)phenoxy]hexanoate (2)

4-Methoxy-4′-hydroazobenzene (**1**) (10.3 g, 47.4 mmol) was dissolved in dry DMF (120 ml). Potassium carbonate (16.7 g, 120.8 mmol), potassium iodide (trace) and methyl 6-bromohexanoate (12.4 g, 59.3 mmol) were added and the mixture warmed to 85–95 °C for *ca.* 20 h. TLC indicated complete conversion to a single product. The reaction was cooled in ice and HCl solution (2 м, 250 ml) was added, to precipitate the product as a fine orange solid. The product was filtered, washed well with cold water and dried (yield: 15.9 g, 94%). Mp 98.4–104.7 °C; ν_{max}/cm^{-1} 1742s, 1601, 1581, and 1497; δ_H(400 MHz) 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d with fine splittings (wfs), J_{ortho} 8.8], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 8.8], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 6.98 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 4.03 [2H (H_{11}), t, $J_{11,10}$ 6.6], 3.88 [3H (CH_3–O)], 3.68 [3H (CH_3–O), s], 2.36 [2H (H_7), t, $J_{7,8}$ 7.6], 1.86–1.80 [2H (H_{10}), m], 1.76–1.69 [2H (H_8), m] and 1.56–1.49 [2H (H_9), m]; δ_C(100 MHz) 174.08, 161.52, 161.06, 147.07, 146.94, 124.32, 114.63, 114.15, 67.92, 55.56, 51.55, 33.98, 28.90, 25.64 and 24.69; *m*/*z* 356 (M+), 325, 221, 129, 107 (100%), 69, 55 and 41 (Found: M^+, 356.1736. Calc. for $C_{20}H_{24}N_2O_4$: *M*, 356.1736).

6-[4-(4-Methoxyphenylazo)phenoxy]hexanoic acid 3

The methyl ester (**2**) (14.4 g, 40.0 mmol) was dissolved in 1,4-dioxan (400 ml) and stirred with NaOH solution (2 м, 100 ml, five-fold excess) for 20 h; the mixture was then heated to reflux for 1 h and allowed to cool. Acidification with 2 м HCl afforded the free acid as a fine yellow precipitate which was filtered, washed well with cold water, dried at the pump and then *in vacuo* at 70 °C over $CaSO_4$, to yield a dry yellow solid (yield: 13.1 g, 96%). Phase behaviour: C 153.9 N 160.0 I (Found: C, 63.70; H, 6.26; N, 8.11. $C_{19}H_{22}N_2O_4$ requires C, 66.65; H, 6.48; N, 8.18%); ν_{max}/cm^{-1} 3409–2600, 1714, 1598, 1582 and 1501; δ_H(400 MHz, [$^2H_6$]DMSO) 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 8.8], 7.85 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 8.8], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 6.98 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 4.04 [2H (H_{11}), t, $J_{11,10}$ 6.6], 3.89 [3H (CH_3–O)], 2.34 [2H (H_7), t, $J_{7,8}$ 7.6], 1.88–1.81 [2H (H_{10}), m], 1.75–1.68 [2H (H_8), m] and 1.58–1.52 [2H (H_9), m]; δ_C(100 MHz; $CDCl_3$ [$^2H_6$]DMSO) 175.44, 161.18, 160.80, 146.64, 146.48, 123.96, 114.33, 113.83, 67.67, 55.24, 33.73, 28.59, 25.28 and 24.33 (Found: M^+, 342.1580. Calc. for $C_{19}H_{22}N_2O_4$: *M*, 342.1580).

N-Benzenesulfonyl-3-(6-bromohexanoyl)pyrrole (9A)

Anhydrous aluminium chloride (10.8 g, 81.1 mmol) was added to dry dichloromethane (200 ml) and stirred under a nitrogen atmosphere. 6-Bromohexanoyl chloride (15.0 g, 70.3 mmol) in dichloromethane (150 ml) was added dropwise at 20 °C and the solution allowed to stir for 30 min. **5A** (11.3 g, 54.5 mmol) in CH_2Cl_2 (150 ml) was slowly added dropwise, keeping the temperature below 5 °C, and the reaction left to stir under a nitrogen atmosphere for *ca.* 20 h. The reaction mixture was carefully hydrolysed with ice–water and the aqueous layer extracted with CH_2Cl_2 (3 portions). The organics were washed with brine and dried over anhydrous magnesium sulfate; filtration followed by evaporation of the solvent yielded a dark brown oil which crystallised upon standing. Recrystallisation was from methanol (yield: 17.3 g, 83%). Mp 53–54.5 °C (Found: C, 50.04; H, 4.78; N, 3.62; Br, 20.64. $C_{16}H_{18}NO_3SBr$ requires: C, 50.01; H, 4.72; N, 3.64; Br, 20.83%); ν_{max}/cm^{-1} 3139m, 3105w, 1672s, 1544m; δ_H(220 MHz) 7.93–7.90 [2H ($H_{2',6'}$), d, $J_{2'3'=6'5'}$ 7.7], 7.75–7.69 [1H (H_2), m], 7.67–7.47 [3H ($H_{3',4',5'}$), m], 7.16–7.09 [1H (H_5), overlapping dd], 6.71–6.65 [1H (H_4), m], 3.39 [2H (H_{11}), t, $J_{11,10}$ 6.6], 2.73 [2H (H_7), t, $J_{7,8}$ 7.7], 1.95–1.79 [2H (H_{10}), m], 1.79–1.61 [2H (H_8), m] and 1.57–1.41 [2H (H_9), m]; *m*/*z* (CI) 386 [$(M + H)^+$, ^{81}Br], 384 [$(M + H)^+$, ^{79}Br], 249, 234, 141, 94, 77 (100%) and 51.

3-(6-Bromohexanoyl)pyrrole (10)

9A (12.0 g, 31.3 mmol) was added to a mixture of 1,4-dioxan (300 ml) and NaOH solution (5 м, 300 ml) and stirred at

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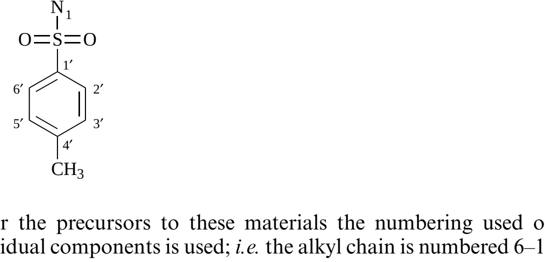
† To avoid complications, we have used an internally consistent numbering system to describe the positions obtained from NMR spectroscopy on these multi-ringed materials as follows:



For the precursors to these materials the numbering used on the individual components is used; *i.e.* the alkyl chain is numbered 6–11, the arylsulfonate ring 1′–6′, *etc.*

room temperature for periods between 48 and 72 h. TLC indicated one major and one minor product. The dioxan was removed and the pale yellow solid re-dissolved in CH_2Cl_2. The aqueous layer was extracted with further portions of CH_2Cl_2 and the organics washed with saturated NaCl solution. After drying and filtering, the solvent was removed to yield a pale yellow oil which crystallised on cooling. The solid was purified using column chromatography on neutral alumina (washed with water 10% w/v) using diethyl ether and light petroleum (1:1) to elute the solid product (crude yield: 8.0 g, 100%). Recrystallisation from diethyl ether–light petroleum (60–80 °C fraction) gave white crystals. Mp 73.5–76 °C; (Found: C, 50.21; H, 5.95; N, 5.79; Br, 31.63. $C_{10}H_{14}NOBr$ requires: C, 49.20; H, 5.78; N, 5.74; Br, 32.73%); ν_{max}/cm^{-1} 3418, 3199–3036, 1734, 1548 and 1505; δ_H(400 MHz) 9.6–9.3 [1H (H_1), br s], 7.45–7.44 [1H (H_2), overlapping ddd, $J_{2,1}$ 3.1 and $J_{2,4=2,5}$ 1.7], 6.80–6.79 [1H (H_5), m], 6.66–6.64 [1H (H_4), m], 3.41 [2H (H_{11}), t, $J_{11,10}$ 6.9], 2.80 [2H, (H_7), t, $J_{7,8}$ 7.3], 1.92–1.85 [2H (H_{10}), m], 1.78–1.71 [2H (H_8), m] and 1.55–1.47 [2H (H_9), m]; δ_C(100 MHz) 196.73 (6-C), 125.63 (3-C), 123.36 (2-C), 119.65 (5-C), 108.55 (4-C), 39.27, 33.73, 32.54, 27.90 and 23.97; *m/z* (CI) 246 [$(M + H)^+$, ^{81}Br], 244 [$(M + H)^+$, ^{79}Br (100%)], 164, 122, 109 and 94; (Found: M^+, 243.0258 (^{79}Br) and 245.0238 (^{81}Br). Calc. for $C_{10}H_{14}NOBr$: *M*, 243.0260 (^{79}Br) and 245.0240 (^{81}Br).

N-Tosyl-3-{6-[4-methoxyphenylazo)phenoxy]hexanoyl}pyrrole (6)

Method 1: Friedel–Craft's acylation of *N*-tosylpyrrole (5). The following method was found to be the correct procedure for the controlled production of the 3-isomer (see Table 1).

Formation of the acid chloride (**4**).—6-[4-(4-Methoxyphenylazo)phenoxy]hexanoic acid (**3**) (6.1 g, 17.8 mmol) was added to thionyl chloride (50 ml, excess) and DMF (trace) and stirred until reaction was complete (checked *via* IR of reaction solution between dry KBr plates; ν_{max} 1795 cm^{-1}). Excess $SOCl_2$ was thoroughly removed under vacuum to yield a red solid.

Friedel–Craft's acylation.—Crushed aluminium chloride (5.0 g, 37.5 mmol) was added to dry CH_2Cl_2 (50 ml) and stirred under a nitrogen atmosphere. The acid chloride **4** in CH_2Cl_2 (150 ml) was added slowly to the reaction at 25 °C over a period of 30 min and then allowed to stand for a further 15 min. (**5**) (3.0 g, 13.6 mmol) in CH_2Cl_2 (20 ml) was added in portions (*ca.* 5 ml) at room temperature, checking the state of the reaction after each new addition by TLC; rapid, clean formation of a single product was indicated. The reaction was allowed to stir overnight and then hydrolysed with ice–water. The organics were extracted with CH_2Cl_2 and the combined extracts washed with brine. Drying and removal of the solvent yielded a dark brown oil which crystallised on cooling and was used without further purification.

Method 2: Williamson etherification of *N*-tosyl-3-(6-bromohexanoyl)pyrrole (9) and 4-methoxy-4′hydroxyazobenzene (1). The pyrrole **9** (22.6 g, 61.8 mmol), **1** (13.5 g, 59.2 mol), anhydrous K_2CO_3 (24.0 g, 174.0 mmol) and KI (trace) were added to DMF (150 ml) and warmed to 90 °C. TLC indicated complete conversion to three products within 90 min. Comparison with known TLC samples showed the middle and lower running spots to be the title compound **6** and 3-{6-[4-(4-methoxyphenylazo)phenoxy]hexanoyl}pyrrole (**7**) respectively. The highest running spot was later determined to be 4-methoxy-4′-toluene-*p*-sulfonyloxy)azobenzene (**13**). The reaction mixture was diluted greatly with water and the organics extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and the solvent removed to yield a reddish-brown solid residue. Flash column chromatography on silica afforded small quantities (*ca.* 2 g each) of the pure highest running and the middle compound, as orange and yellow crystals, respectively; the lowest running compound was not isolated in the pure form. The isolated compounds were characterised and assigned as follows.

N-tosyl-3-{6-[4-(4-*methoxyphenylazo*)*phenoxy*]*hexanoyl*}-*pyrrole* (**6**).—Mp 128.8 °C (Found: C, 66.03; H, 5.75; N, 7.54; S, 5.48. $C_{30}H_{31}N_3O_5S$ requires: C, 66.04; H, 5.73; N, 7.70 S, 5.88%); ν_{max}/cm^{-1} 3120w, 3102w, 1670s, 1600s, 1581s, 1542m and 1502s; δ_H(400 MHz) 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), dd, J_{ortho} 9.3 and J_{para} 2.2], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), dd, J_{ortho} 9.3 and J_{para} 2.2], 7.80 [2H ($H_{2',6'}$), d, $J_{2',3'=6'5'}$ 8.1], 7.73 [1H (H_2) overlapping dd, $J_{2,4}$ 2.0 and $J_{2,5}$ 2.0], 7.33 [2H ($H_{3',5'}$), br d, $J_{3'2'=5'6'}$ 8.1], 7.13 [1H (H_5), dd, $J_{5,4}$ 3.2 and $J_{5,2}$ 2.0], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), dd, J_{ortho} 9.3 and J_{para} 2.2], 6.98 [2H ($H_{13,17}$ or $H_{20,22}$), dd, J_{ortho} 9.3 and J_{para} 2.2], 6.68 [1H (H_4), dd, $J_{4,5}$ 3.2 and $J_{4,2}$ 2.0], 4.03 [2H, (H_{11}), t, $J_{11,10}$ 6.4], 3.88 [3H (CH_3–O), s], 2.77 [2H (H_7), t, $J_{7,8}$ 7.3], 2.41 [3H (Ar–CH_3) s], 1.86–1.73 [4H (H_{10} and H_8), overlapping ms], and 1.58–1.52 [2H (H_9), m]; δ_C(100 MHz) 195.30, 161.52, 161.08, 147.07, 146.94, 145.98, 135.11, 130.34, 129.00, 127.23, 124.32 (overlapping signals), 124.08, 121.54, 114.65, 114.15, 112.36, 67.98, 55.56, 39.54, 29.08, 25.79, 23.92 and 21.71 (Found: M^+, 545.1986. Calc. for $C_{30}H_{31}N_3O_5S$: *M*, 545.1984).

4-*Methoxy*-4′-(*toluene*-p-*sulfonyloxy*)*azobenzene* (**13**).—Mp 131.4 °C; ν_{max}/cm^{-1} 1605, 1585 and 1502; δ_H(400 MHz) 7.89 [2H ($H_{19,23}$ or $H_{14,16}$) d wfs, J_{ortho} 8.8], 7.79 [2H ($H_{19,23}$ or $H_{14,16}$), d wfs, J_{ortho} 8.8], 7.72 [2H ($H_{2'6'}$), d wfs, $J_{2'3'=6'5'}$ 8.3], 7.31 [2H ($H_{3'5'}$), br d, $J_{3'2'=6'5'}$ 8.3], 7.10 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 3.88 [3H (CH_3O), s] and 2.44 [3H (Ar–CH_3), s]; δ_C(100 MHz) 162.36, 151.01, 150.71, 146.76, 145.54, 132.13, 129.83, 128.56, 124.91, 123.74, 123.02, 114.26, 55.60 and 21.73 (Found: M^+, 382.0988. Calc. for $C_{20}H_{18}N_2SO_4$: *M*, 382.0987).

N-Tosyl-2-{6-[4-(4-methoxyphenylazo)phenoxy]hexanoyl}-pyrrole (6α)

The 2-isomer was obtained by the following procedure. The acid chloride **4** (15.9 g, 44.2 mmol) in CH_2Cl_2 (150 ml) was added to $AlCl_3$ (7.8 g, 58.5 mmol) in CH_2Cl_2 (50 ml) at 20 °C and allowed to stir for 30 min. *N*-Tosylpyrrole (**5**) (6.5 g, 29.5 mmol) in CH_2Cl_2 (60 ml) was added slowly, keeping the temperature below −5 °C; the reaction was allowed to reach ambient temperature and stirred for 5 days. TLC indicated at least five compounds present, including unreacted **5**. Work-up yielded 17.7 g of crude product. A similar preparation to this, commencing with **5A** (4.3 g, 29.3 mmol), gave 11.8 g (76%) of crude product containing one major (2-isomer) and one minor compound, with no starting material present.

A small portion was purified by flash column chromatography on silica, using diethyl ether and light petroleum (graded elution) as eluant. Pure, yellow–orange, needle-like crystals of **6α** precipitated from solution; these were filtered with washing and dried at the pump. Phase behaviour: C_1 122 C_2 140 I; ν_{max}/cm^{-1}, 1678, 1600, 1581, 1503 and 1255; δ_H(400 MHz) 7.90 [2H ($H_{2'6}$), $J_{2'3'=6'5'}$ 8.4], 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.80–7.79 [1H (H_5), dd], 7.31 [2H ($H_{3',5'}$) br d, $J_{3'2'=5'6'}$ 8.4]. 7.04–7.03 [1H (H_3), dd], 7.00 2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 9.2], 6.96 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 9.2], 6.33–6.32 [1H (H_4), overlapping dd], 4.00 [2H (H_{11}), t, $J_{11,10}$ 6.4], 3.88 [3H (CH_3–O), s], 2.72 [2H (H_7), t, $J_{7,8}$ 7.5], 2.41 [3H (Ar–CH_3), s], 1.83–1.76 [2H (H_{10}), m, 5 lines], 1.74–1.67 [2H (H_8), m, 5 lines] and 1.51–1.43 [2H (H_9), m]; δ_C(100 MHz) 188.8, 161.5, 161.0, 147.1, 146.9, 144.7, 136.0, 133.3, 130.1, 129.3, 128.3, 124.3, 123.2, 114.6, 114.1, 110.2, 67.9, 55.5, 39.2, 29.0, 25.6, 24.4 and 21.7; *m/z* (EI) 544 ($M\text{-}1^+$, 100%), 316, 135, 107, 91, 69 and 28 (Found: M^+, 545.1990. Calc. for $C_{30}H_{31}N_3O_5S$: *M*, 545.1984).

3-{6-[4-(4-Methoxyphenylazo)phenoxy]hexanoyl}pyrrole 7

The crude product **6** was added to ethanol (300 ml) and KOH solution (5 M, 300 ml) and heated under reflux for 1 h. TLC indicated complete conversion to the product. The ethanol was removed under vacuum and the orange precipitate redissolved in ethyl acetate; some insoluble polymeric residue was removed from solution. The organics were extracted with ethyl acetate (5 portions) and the combined organics washed with brine, dried and the solvent removed to yield an orange–brown solid [yield: 4.7 g, 67.6%; based on **5**]. Recrystallisation from ethanol–water furnished small orange crystals. Mp 147.2–150.2 °C (Found: C, 68.17; H, 6.08; N, 9.79. $C_{23}H_{25}N_3O_3$ requires: C, 70.57; H, 6.44; N, 10.73%); ν_{max}/cm^{-1}, 3203, 1639, 1600, 1579 and 1501; δ_H(400 MHz) 8.6–8.5 [1H (H_1), br s], 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.44–7.42 [1H (H_2), m], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 9.2], 6.98 [1H (H_2), d wfs, J_{ortho} 9.2], 6.80–6.78 [1H (H_5), m], 6.69–6.67 [1H (H_4), m], 4.04 [2H (H_{11}), t, $J_{11,10}$ 6.4], 3.89 [3H (CH_3–O), s], 2.81 [2H (H_7), t, $J_{7,8}$ 7.5], 1.90–1.78 [4H (H_8 and H_{10}), m] and 1.61–1.53 [2H (H_9), m]; δ_C(100 MHz) 196.18, 161.50, 161.14, 147.09, 146.91, 126.08, 124.32, 122.84, 119.29, 114.65, 114.14, 108.87, 96.12, 68.07, 55.54, 39.50, 29.11, 25.91 and 24.54; *m*/*z* (EI) 391 (M^+), 342, 228, 164, 135, 122, 107, 94 (100%), 77 and 66 (Found: M^+, 391.1896. Calc. for $C_{23}H_{25}N_3O_3$: *M*, 391.1896).

2-{6-[4-(4-Methoxyphenylazo)phenoxy]hexanoyl}pyrrole (7α)

The 2-isomer **7α** was obtained from its precursor **6α** (11.8 g) by a similar method to the one described for **7**, using NaOH solution (5 M, 350 ml) and 1,4-dioxan (350 ml). Work-up gave a yellow solid which was recrystallised from ethanol (yield: 4.2 g, 47.9%). Mp 119.9–126.2 °C (Found: C, 69.70; H, 6.36; N, 10.45. $C_{23}H_{25}N_3O_3$ requires: C, 70.57; H, 6.44; N, 10.23%); ν_{max}/cm^{-1} 3269m, 1642, 1595, 1579 and 1498; δ_H(250 MHz) 9.45 [1H (H_1), br s], 7.89 [2H ($H_{14,16}$ or $H_{19,23}$), d, J_{ortho} 9.0], 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d, J_{ortho} 9.0], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d, J_{ortho} 9.0], 6.98 [2H ($H_{13,17}$ or $H_{20,22}$), d, J_{ortho} 8.89], 7.05–7.01 [1H (H_5), m], 6.95–6.92 [1H (H_3), m], 6.30–6.26 [1H (H_4), m], 4.03 [2H (H_{11}), t, $J_{11,10}$ 6.4], 3.90 [3H (CH_3–O), s], 2.83 [2H (H_7), t, $J_{7,8}$ 7.4], 1.92–1.77 [4H (H_8 or H_{10}), overlapping ms] and 1.64–1.51 [2H (H_9), m]; δ_C(63 MHz) 190.77, 161.53, 161.11, 147.13, 146.98, 132.00, 124.73, 124.32, 116.28, 114.69, 114.18, 110.56, 68.06, 55.53, 37.80, 29.09, 25.92 and 24.93; *m*/*z* (EI) 391 (M^+), 164, 122, 107, 94 (100%), 77 and 66 (Found: M^+, 391.1896. Calc. for $C_{23}H_{25}N_3O_3$: *M*, 391.1896).

3-{6-[4-(4-Methoxyphenylazo)phenoxy]hexyl}pyrrole (8)

The acylpyrrole **7** (4.7 g, 12 mmol) was added to propan-2-ol containing sodium borohydride (7.2 g, 16-fold excess) and refluxed for *ca.* 40 h, during which time complete conversion to the product occurred. The reaction was diluted with water and most of the propan-2-ol removed under vacuum. The organics were extracted with CH_2Cl_2 (three portions), dried and the solvent removed to yield a dark orange, oily residue. The crude product was redissolved in the minimum amount of CH_2Cl_2 and pulled under suction through a bed of silica to remove any polymeric residues. Removal of the solvent gave a much cleaner, orange–brown solid which was recrystallised from ethanol (yield: 0.8 g, 17.7%). Phase behaviour: C 98 N (77.3–75.0) I (Found: C, 71.66; H, 6.87; N, 10.86. $C_{23}H_{27}N_3O_2$ requires: C, 73.18; H, 7.21; N, 11.73%); ν_{max}/cm^{-1} 3401, 1601, 1581 and 1496; (CH_2Cl_2) λ_{max}/nm 358.4 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 16 698) and 240.0 (14 256), respectively; δ_H(400 MHz) 8.1–7.9 [1H (H_1), br s], 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 9.2], 7.00 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 9.2], 6.98 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 9.2], 6.72 [1H (H_5), dd, $J_{5,4}$ 4.8 and $J_{5,1}$ 2.6], 6.58–6.57 [1H (H_2), m], 6.10–6.09 [1H (H_4), m], 4.02 [2H (H_{11}), t, $J_{11,10}$ 6.6], 3.88 [3H (CH_3–O), s], 2.51 [2H (H_6), t, $J_{6,7}$ 7.7], 1.84–1.79 [2H (H_{10}), m, 5 lines], 1.67–1.59 [2H (H_7), m, 5 lines] and 1.56–1.37 [4H (H_8 and H_9), overlapping ms]; δ_C(100 MHz) 161.48, 161.21, 147.07, 146.85, 124.30, 117.61, 114.85, 114.65, 114.14, 108.48, 68.29, 55.52, 31.07, 29.68, 29.15, 26.83 and 25.88; *m*/*z* (EI) 377 (M^+), 258, 242, 228, 150, 135, 121, 107, 92 and 80 (100%) (Found: M^+, 377.2103. Calc. for $C_{23}H_{27}N_3O_2$: *M*, 377.2103).

2-{6-[4-(4-Methoxyphenylazo)phenoxy]hexyl}pyrrole (8α)

The procedure described above for the preparation of **8** was repeated with the 2-substituted derivative. Phase behaviour: C 108.7–110.7 N (52.3–48.7) I; ν_{max}/cm^{-1} 3363, 1604, 1584 and 1499; δ_H(400 MHz) 7.87 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs J_{ortho} 8.8], 7.86 [2H ($H_{14,16}$ or $H_{19,23}$), d wfs, J_{ortho} 8.8], 6.99 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 6.97 [2H ($H_{13,17}$ or $H_{20,22}$), d wfs, J_{ortho} 8.8], 6.66–6.64 [1H (H_5), overlapping dd, $J_{5,1}$ 2.5 and $J_{5,4}$ 2.5], 6.14–6.12 [1H (H_4), overlapping dd, $J_{4,3}$ 3.5 and $J_{4,5}$ 2.5], 5.92 [1H (H_3), br m], 4.01 [2H (H_{11}), t, $J_{11,10}$ 6.6], 3.87 [3H (CH_3–O), s], 2.61 [2H (H_6), t, $J_{6,7}$ 7.7], 1.83–1.77 [2H (H_{10}), m, 5 lines], 1.70–1.62 [2H (H_7), m, 5 lines] and 1.51–1.43 [4H (H_8 and H_9), overlapping ms]; δ_C(100 MHz) 161.80, 161.41, 147.37, 147.20, 127.82, 124.60, 116.33, 114.92, 114.43, 108.54, 105.23, 68.44, 55.82, 29.85, 29.39, 29.28, 27.89 and 26.10; *m*/*z* (EI) 377 (M^+), 255, 241, 228, 135, 121, 107, 92 and 80 (100%) (Found: M^+, 377.2106. Calc. for $C_{23}H_{27}N_3O_2$: *M*, 377.2103).

3-[6-(4′-Cyanobiphenyl-4-yloxy)hexanoyl]pyrrole (11)

3-(6-Bromohexanoyl)pyrrole (**10**) (8.00 g, 32.8 mmol), 4-cyano-4′-hydroxybiphenyl (6.39 g, 32.7 mmol), anhydrous potassium carbonate (13.83 g, 100.0 mmol) and potassium iodide (trace) were added to DMF (165 ml) and warmed to 90–100 °C for 1 h. TLC indicated complete conversion to one major and one very minor product. The product was precipitated from solution by the addition of a large excess of demin. water and filtered at the pump, washing well with water. The cream solid was dried at the pump and then *in vacuo* over P_2O_5 at 65 °C overnight. The crude product (yield: 10.1 g, 86.0%) was recrystallised from propan-2-ol–water. Mp 131.0 °C; (Found: C, 76.88; H, 6.27; N, 7.66. $C_{23}H_{22}N_2O_2$ requires: C, 77.07; H, 6.19; N, 7.82%); ν_{max}/cm^{-1} 3379, 3203m, 2227, 1641, 1601 and 1495; δ_H(250 MHz) 7.68 [2H ($H_{20,22}$), d wfs, $J_{20,19=22,23}$ 8.6], 7.64 [2H ($H_{19,23}$), d wfs, $J_{19,20=23,22}$ 8.6], 7.54 [2H ($H_{14,16}$), d wfs, $J_{14,13=16,17}$ 8.9], 7.47–7.41 [1H (H_2), m, 5 lines], 6.98 [2H ($H_{13,17}$), d wfs, $J_{13,14=17,16}$ 8.9], 6.82–6.76 [1H (H_5), m, 5 lines], 6.71–6.64 [1H (H_4), m, 6 lines], 4.02 [2H (H_{11}), t, $J_{11,10}$ 6.5], 2.81 [2H (H_7), t, $J_{7,8}$ 7.3], 1.93–1.72 [4H (H_8 and H_{10}), overlapping ms] and 1.69–1.48 [2H (H_9), m]; δ_C(63 MHz) 196.11, 159.76, 145.32, 132.54, 131.33, 128.30, 127.07, 122.80, 119.29, 119.08, 115.15, 110.07, 108.86, 68.00, 39.52, 29.15, 25.96 and 24.53; *m*/*z* (EI) 358 (M^+), 195, 164, 122, 109, 94 (100%), 67 and 55; (Found: M^+, 358.1680. Calc. for $C_{23}H_{22}N_2O_2$: *M*, 358.1681).

3-[6-(4′-Cyanobiphenyl-4-yloxy)hexyl]pyrrole (12)

The acylpyrrole (**11**) (4.64 g, 13.0 mmol) and $NaBH_4$ (5.29 g, 139.8 mmol) were added to propan-2-ol (150 ml) and refluxed for 48 h. The reaction was carefully hydrolysed with water and the solvent was removed; the crude residue was redissolved in ethyl acetate and the organics extracted into the organic layer (three times) with fresh solvent. The combined organics were dried over $MgSO_4$ and filtered. Removal of solvent yielded the crude product as a cream solid (yield: 2.9 g, 65.5%). The crude material was redissolved in CH_2Cl_2 and passed through a bed of silica to remove polymeric residues. Recrystallisation of the cleaner product from EtOA–light petroleum (60–80 °C fraction) furnished the desired compound as white crystals (yield: 2.5 g, 56.1%) which were dried *in vacuo*. Phase behaviour: C_1 86.0 C_2 96.6 N (72.4–72.0) I; (Found: C, 79.55; H, 6.70; N, 8.08. $C_{23}H_{24}N_2O$ requires: C, 80.20; H, 7.02; N, 8.13%); ν_{max}/cm^{-1} 3441, 3369, 2231, 1604, 1582, 1552, 1521 and 1496; δ_H(400 MHz) 8.00 [1H (H_1), br s], 7.68 [2H ($H_{20,22}$), d wfs, $J_{20,19=22,23}$ 8.4], 7.64 [2H ($H_{19,23}$), d wfs, $J_{19,20=23,22}$ 8.4 and $J_{19,22=23,20}$ 1.8], 7.53 [2H ($H_{14,16}$), d wfs, $J_{14,13=16,17}$ 8.8], 6.99 [2H ($H_{13,17}$), d wfs, $J_{13,14=17,16}$ 8.8], 6.74–6.72 [1H (H_5), m], 6.59–6.58 [1H (H_2), m], 6.11–6.09 [1H (H_4), m, 5 lines], 4.01 [2H (H_{11}), t, $J_{11,10}$ 6.6], 2.51

[2H (H_7), t, $J_{7,8}$ 7.7], 1.86–1.79 [2H (H_{10}), m, 5 lines], 1.66–1.59 [2H (H_7), m] and 1.56–1.40 [4H (H_8 and H_9), overlapping ms]; δ_C(63 MHz) 159.81, 145.29, 132.51, 131.24, 128.27, 127.04, 124.39, 119.07, 117.59, 115.12, 114.83, 110.04, 108.52, 68.20, 31.11, 29.20, 26.87 and 25.93; *m/z* (EI) 344 (M^+), 208, 195, 166, 150, 80 (100%), 94 and 67 (Found: 344.1886. Calc. for $C_{23}H_{24}N_2O$: *M*, 344.1889).

Chemical polymerisation of 3-[6-(4′-cyanobiphenyl-4-yloxy)-hexyl]pyrrole (12)

Method 1: using copper(II) perchlorate. The pyrrole derivative (**12**) (1 mmol or 1 equiv.) was dissolved in acetonitrile (8–10 ml) and added to a reaction vessel, maintained under a continuous stream of nitrogen and held at 20 ± 1 °C in a thermostatted water bath. Copper(II) perchlorate hexahydrate, $Cu(ClO_4)_2\cdot 6H_2O$ (2 mmol or equiv.) was dissolved in acetonitrile (8–10 ml) and added dropwise to the monomer solution. A black precipitate was formed immediately in the clear solution. The mixture was allowed to stir for a minimum of 90 min (sometimes up to 20 h) before the reaction was filtered.

The solid polymers were washed under filtration with copious amounts of water and then acetonitrile, in order to remove unreacted monomer and oxidant. The polymers were further washed with hot acetonitrile using a continuous Soxhlet extractor for up to 6–8 h. Drying *in vacuo* for a further 6–8 h yielded amorphous black solids for polypyrrole and poly-3-[6-(4′-cyanobiphenyl-4-yloxy)hexyl]pyrrole [poly(**12**)].

Method 2: using ferric chloride. All solvents and reagents were thoroughly degassed prior to use as follows: the solution was treated for 30 min in an ultrasonic bath followed by 60–90 min bubbling with nitrogen, in a flask fitted with a Suba•Seal and outlet needle. Thereafter, the solvents were kept under nitrogen at all times; subsequent manipulations of solvents were performed with nitrogen-purged syringes and/or a cannula, through degassed, Suba•Sealed flasks.

A three-necked flask equipped with a Suba•Seal, two-way tap and filter stick (sealed at its open end with a small Suba•Seal) was charged with a magnetic follower, anhydrous ferric chloride (0.27 g) and evacuated repeatedly (five times) under high vacuum and refilled with nitrogen, using a double-manifold system. Degassed MeCN (HPLC grade, 20 ml) was added *via* a syringe. The monomer (which was in an evacuated flask and degassed as before, 0.19 g) in MeCN (20 ml) was added to the reaction flask as a slurry or solution in MeCN and stirred. A black precipitate formed within minutes and was stirred for a further *ca.* 17–18 h.

The polymeric solids were washed as follows: the reaction solvent was removed under vacuum through a cannula, inserted into the filter stick and whose other end was inserted into a clean, dry, degassed flask, connected to the pump. The remaining polymeric solids were washed with degassed water (three portions) followed by degassed acetone or acetonitrile (two portions), and filtered in a similar manner. The washed polymers were dried under vacuum for 2–3 h.

Method 3: polymerisation of aligned monomer. The apparatus for polymerising the mesogenic pyrroles (and non-mesogenic pyrroles) consisted basically of a reaction cell through which bromine vapour could be passed. This apparatus was designed to fit within the cavity of a Swift polarising microscope and contained an aperture for viewing the sample to ensure the required phase/alignment state had been achieved. The reaction cell consisted of a small glass vessel equipped with an inlet and outlet, to permit the throughput of oxidant vapour and nitrogen (as a carrier gas). The cell was designed to fit within a two-piece aluminium heating block, shaped out to contain the cell and fitted with four heating elements, connected to a 10 A power supply. Both halves of the heating block contained a small aperture, orthogonal to the plane of, and positioned above and below, the cell centre. This permitted the passage of light through the cell to the eyepiece lens. The temperature of the cell was regulated with a temperature controller, connected to the cell *via* a Type K Chromel-Aluminel thermocouple, inserted into a small aperture within the heating block.

A glass slide (*ca.* 1 × 1 cm) was spin-coated with a solution of Probimide® 32 in DMF, a polyimide precursor. This was annealed at high temperatures (*ca.* 200 °C), followed by unidirectional rubbing with a soft cloth, to yield a hard, inert, rubbed polymer film, suitable for enticing homogeneous alignment of a mesophase. The sample to be polymerised [(**12**), *ca.* 50 mg] was deposited on the glass slide and placed in the cell cavity and the cell was purged with a continuous stream of nitrogen. The cell was heated to the approximate required temperature (the heating block was not calibrated), which was normally taken to be either in the middle of the range for mesophase formation, or *ca.* 10 °C above the clearing point, depending on the nature of the polymer required. Once the sample was in the required phase (determined *via* microscopy), the cell was purged with a continuous stream of bromine–nitrogen vapour. The cell was then re-purged with fresh nitrogen alone, cooled and the glass slide containing the polymeric deposit removed. The samples were washed (still attached to the glass slide) in acetonitrile for 24 h and dried *in vacuo* for 3–4 h.

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