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Conformational changes in regioregular polythiophenes due to thermal crosslinking

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Regioregular polythiophene copolymers **10a–d** containing hexyl and 11-hydroxyundecyl side chains have been synthesised, by nickel-catalysed cross-coupling of well-defined Grignard intermediates. The hydroxy groups were protected during the polymerisation as tetrahydropyranyl ethers, and subsequently transformed into azide groups. These azide-functionalised copolymers **11a–d** were heated under vacuum, leading to azide decomposition, nitrene formation and crosslinking. The resultant polymer films showed decreased solubility (or insolubility) and a shift in the absorption spectrum to shorter wavelengths dependent on the azide content of the polymer. This colour change is rationalised in terms of the conformational change in the polythiophene backbone, associated with thermochromism, which has been partially fixed by the crosslinking at high temperature. This is supported by the modified thermochromism and photoluminescence behaviour of the crosslinked polymer films.

Substituted polythiophenes form a class of stable and soluble conjugated polymers.[1,2] In common with other conjugated organic polymers, polythiophenes exhibit electroluminescence; this was first observed for poly(3-alkylthiophene)s[3–5] but more recently the flexibility of polythiophenes for fabricating devices covering the whole visible spectrum has been demonstrated.[6–9]

Soluble polythiophenes are most commonly synthesised by chemical oxidative coupling or by electropolymerisation.[2] More recently, routes have been developed which give soluble and ‘regioregular’ poly(3-alkylthiophene)s which contain essentially only head-to-tail links.[10–15] This gives polymers with a better defined structure which can help elucidate structure–property relationships. These routes have been applied to the synthesis of regioregular polythiophenes having a variety of different side chains.[16–20] Electroluminescence in regioregular poly(3-alkylthiophene)s has been reported,[19,21–23] and found to be similar to that of non-regioregular poly(3-alkylthiophene)s.

Polythiophenes are also of interest as a result of their thermochromic[24–27] and solvatochromic[24–26,28] properties in that the colour of a polythiophene is dependent on the temperature and the solvent. Regioregular polythiophenes too have been shown to display thermochromism in solution,[16] solvatochromism,[16,29] and a variety of fascinating chiroptical properties.[25,30–33]

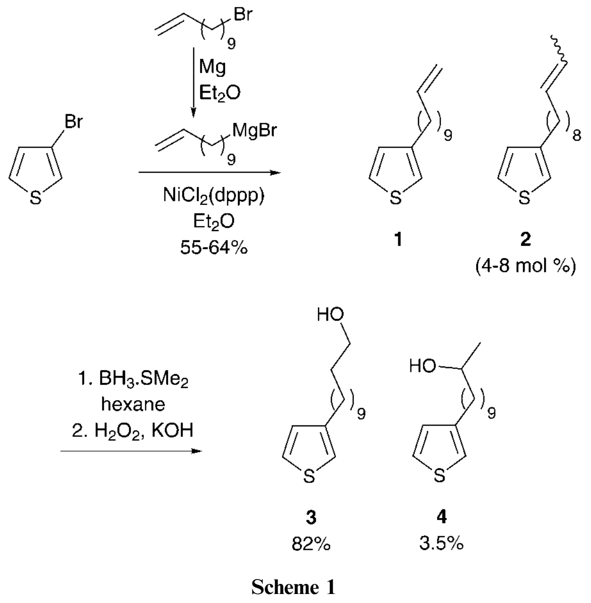
A non-regioregular polythiophene containing methacrylate side chains has recently been reported[34] which could be crosslinked photochemically to give an insoluble polythiophene. Such a solution processible polythiophene which can be rendered insoluble after film formation would greatly facilitate the fabrication of multilayer devices for light emitting diodes.

In this work, *regioregular* polythiophene copolymers consisting mainly of hexyl side chains and having different proportions of 11-hydroxyundecyl side chains have been synthesised. Preliminary results have been reported.[35] The polymerisation route used is that developed by McCullough[14] and the alcohol is protected during this reaction as a tetrahydropyranyl (THP) ether, as has been previously described.[19] These hydroxy groups have been converted to azide groups to allow thermal crosslinking (rather than photochemical crosslinking since the polythiophene might be damaged by ultraviolet light). On heating or irradiation, the azide group, –N_3, decomposes to a highly reactive nitrene, –N:, with the loss of nitrogen.[36,37] This nitrene can then insert into single or double bonds, and in this case onto other side chains or the polymer backbone of different polymer chains, leading to the formation of crosslinks and, if there is sufficient crosslinking, rendering the polymer film insoluble.

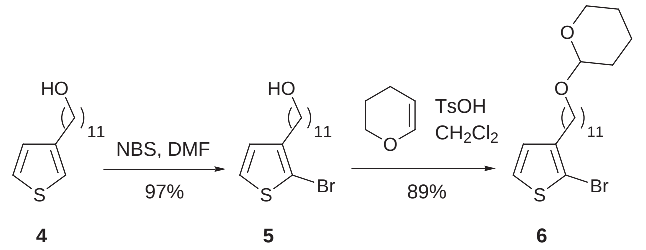
Results and discussion

Monomer synthesis

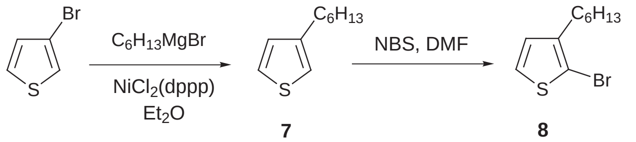
The Grignard reagent derived from 1-bromoundec-10-ene was coupled with 3-bromothiophene with a nickel catalyst[38] to give 3-(undec-10-enyl)thiophene **1**; a small amount of isomerisation was found to take place and 3-(undec-9-enyl)thiophene **2** was also observed (between 4 and 8 mol%) (Scheme 1). Separation of the isomers was not attempted. Hydroboration with borane–dimethyl sulfide,[39] followed by oxidative work-up, gave 3-(11-hydroxyundecyl)thiophene **3** (Scheme 1) and



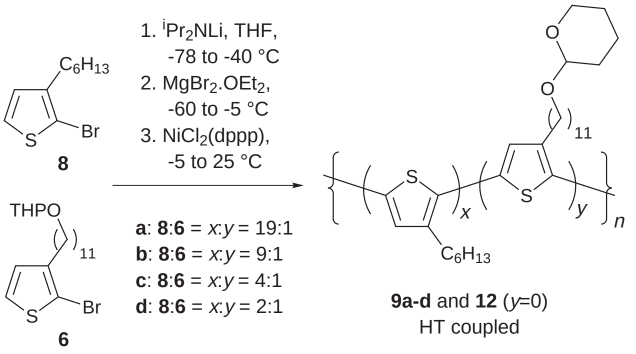
Scheme 1



Scheme 2



Scheme 3



Scheme 4

its regioisomer, 3-(10-hydroxyundecyl)thiophene **4**. The primary alcohol **3** was isolated by column chromatography and was regioselectively monobrominated with *N*-bromosuccinimide in dimethylformamide[40] to afford 2-bromo-3-(11-hydroxyundecyl)thiophene **5** in good yield and with less than 5% unbrominated and dibrominated products (Scheme 2).† Protection with dihydropyran gave the THP protected alcohol **6** (Scheme 2).

3-Hexylthiophene **7** was synthesised by nickel catalysed coupling of hexylmagnesium bromide with 3-bromothiophene.[38,41] Monobromination, with *N*-bromosuccinimide in dimethylformamide,[40] gave 2-bromo-3-hexylthiophene **8** (Scheme 3).

Polymer synthesis

Copolymers, between monomers **6** and **8** in ratios of 1 : 19 to 1 : 2, were synthesised following the polymerisation method of McCullough[14,19] (Scheme 4). The copolymers obtained were regioregular (essentially fully head-to-tail coupled), as seen from their ^{1}H NMR spectra (singlet peak at δ 6.98 ppm). There was negligible cleavage of the tetrahydropyranyl protecting groups and the monomer feed ratio (**6** : **8**) was seen to be closely retained in the copolymer (determined from ^{1}H NMR from intensity of signals due to THP-protected side chains) (Table 1). Polymer yields were low but were comparable with those that had been obtained for regioregular poly(3-hexylthiophene) **12**.

Deprotection of the alcohols was achieved by heating to reflux suspensions of copolymers **9a–d** in acidified methanol (Scheme 5). Complete deprotection was achieved, as determined by ^{1}H NMR, without significantly affecting the ratio of side chains (as determined by ^{1}H NMR, Table 1) or affecting the regioregularity of the polymers. The hydroxy-functionalised copolymers **10a–d** were observed to have diminished solubility (in chloroform), in particular for the 2 : 1 copolymer **10d**. One-step azidation of the copolymers **10a–d** was achieved with diphenylphosphoryl azide, di-*tert*-butyl azodicarboxylate and triphenylphosphine in tetrahydrofuran[42] to give, after isolation by precipitation, the fully azidated copolymers **11a–d** (Scheme 5). For copolymers **11a–c**, the reaction was complete when stopped after the times indicated and the azide content of the copolymers (determined by ^{1}H NMR) was close to that expected (Table 1). Reaction of 2 : 1 copolymer **10d** was far slower, due to the decreased solubility as a result of the high proportion of hydroxy groups, and after 5 days there was only a 25% conversion of alcohols to azides. After a further 33 days, copolymer **11d** was recovered and found to contain 25% azidated side chains (by ^{1}H NMR) and no free alcohol but to have a small amount of unidentified side chains, which might account for the low azide content.‡

Thermal crosslinking

Differential scanning calorimetry of copolymer **11b** indicated that azide decomposition occurred at about 200 °C. Infrared studies of films of copolymer **11d** (25% azide side chains) showed that heating films at 225 °C under vacuum for 30 minutes was sufficient to completely decompose all azide present, but that heating to 200 °C was not quite sufficient. Detailed studies on the heating and crosslinking of copolymers **11a–d** were therefore carried out with heating to 225 °C for 30 minutes as the standard crosslinking conditions.

When all polymer samples were heated to 225 °C [including poly(3-hexylthiophene) **12**, no azide] the colour turned from purple to orange; this thermochromism has been well documented in non-regioregular poly(3-alkylthiophene)s[24,27] and represents a change in polymer conformation from an ordered, more crystalline form with extended conjugation between rings at low temperatures (purple) to a disordered and random form with little conjugation at high temperatures (orange). On cooling, the samples were observed to partially return to their original purple colours; those polymers with higher azide contents were seen to have experienced greater permanent colour changes (Fig. 1). The control sample, regioregular poly(3-hexylthiophene) **12**, did not suffer a permanent colour change. The shift in absorption to shorter wavelengths indicates a shortening of the conjugation along the polymer backbone, and this could be due to a conformational change in the polymer backbone or to an interruption in conjugation by the insertion of nitrenes. However the magnitude of the effect would suggest a conformational change, associated with thermochromism, which has become partially fixed by the crosslinking at high temperatures. It is difficult to be specific about the nature of the crosslinking. Insertion into the thiophene double bond followed by ring rearrangement might be energetically more favourable than C–H insertion.

The crosslinked films from copolymers **11b–d** were found to be completely insoluble in chloroform, tetrahydrofuran and toluene. However, in contact with these solvents, the polymer films showed a shift in the absorption spectrum to shorter wavelengths and became orange: in contact with chloroform all crosslinked samples (from **11a**, **b**, **c** and **d**) showed a peak absorption wavelength of around 460 nm. This is only a little higher than the peak absorption of 450 nm seen for the

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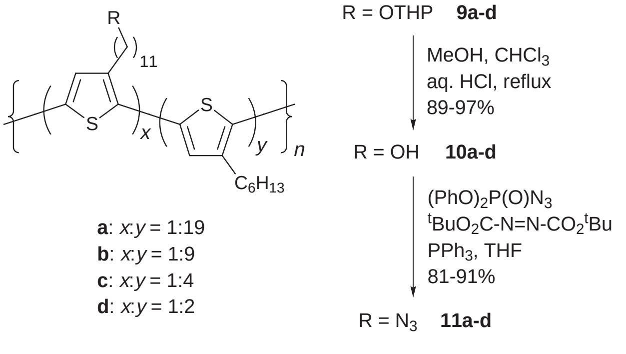
†The unbrominated, monobrominated and dibrominated products could be readily distinguished by ^{1}H NMR spectroscopy with deuterobenzene as solvent.

‡A referee has commented on the apparent rise in M_n and M_w in the conversion of the polymeric THP ether to alcohol to azide. This is not easily explained, except that formation of the azide is probably already accompanied by some small extent of thermally induced crosslinking, which would be expected to increase molar mass.

Table 1 Reactions of copolymers **9a–d** to **11a–d**

Polymer series	Monomer ratio **8**:**6**	Yield of copolymer **9a–d** (%)	% THP side chains in copolymer **9a–d**	% OH side chains in copolymer **10a–d**	% N_3 side chains in copolymer **11a–d**	Azidation reaction time/days
a	19:1	7	3	4	3.5	2
b	9:1	9	9	10	9	5
c	4:1	9	19	20	17	7
d	2:1	18	31	32	25	38



Scheme 5

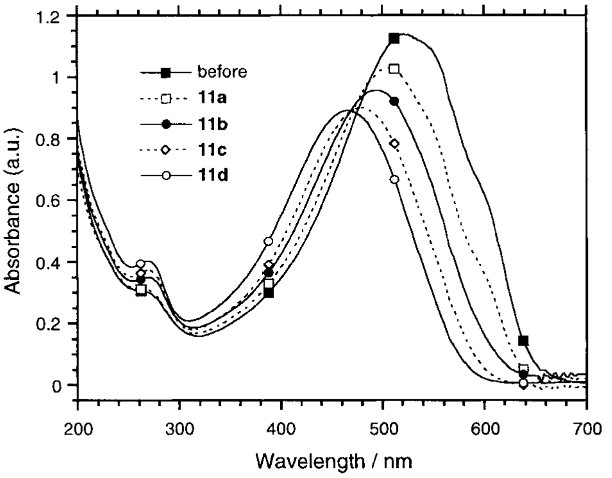


Fig. 1 Absorption spectra of copolymers **11a–d** before and after crosslinking (30 minutes, 225 °C, vacuum).

uncrosslinked polymers **11a–d** in chloroform solution. This is illustrated with a crosslinked§ sample of the 9:1 copolymer **11b** (Fig. 2). Therefore the crosslinked films, although insoluble, still show solvatochromism, as do insoluble gels derived from ferric chloride coupled poly(3-alkylthiophene)s.[43,44] The copolymer **11a** with the lowest azide content (3.5% of side chains), after crosslinking, had a very minor soluble fraction; the remaining polymer, after this washing, was insoluble.

Solutions of regioregular poly(3-hexylthiophene) **12** with the 19:1 copolymer **11a** in chloroform were prepared to give polymer films with lower azide contents (0.9 and 1.6% of side chains). These films, after crosslinking, were only partially insoluble and showed smaller shifts in their absorption spectra. The effect of heating to 225 °C under vacuum for 30 minutes on the peak absorption wavelength of regioregular polythiophenes with different azide contents is summarised (Fig. 3).

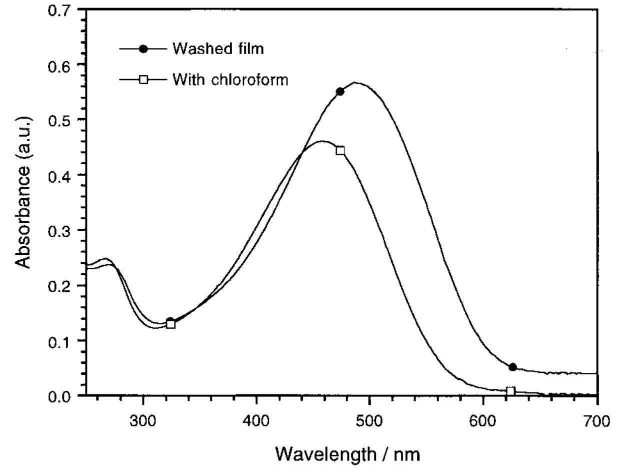


Fig. 2 Absorption spectra of a crosslinked film of copolymer **11b**, dry (after washing) and in contact with chloroform.

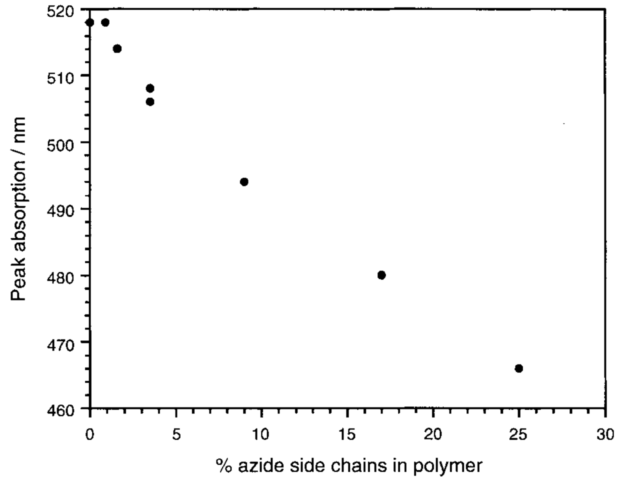


Fig. 3 Peak absorption wavelength of polythiophene copolymers with different azide contents, after heating to 225 °C under vacuum for 30 minutes.

Thermochromism of crosslinked films

Copolymers **11b** and **11d** (9 and 25% azide-substituted side chains respectively) were crosslinked at 225 °C and allowed to cool; a control sample of regioregular poly(3-hexylthiophene) **12** was subjected to the same conditions. Each sample was then heated to about 220 °C (in air) and its absorption spectrum measured (Fig. 4). The absorption spectra of the three polymers at this temperature were closely similar, as were the absorption spectra before crosslinking. This would suggest that the disruption of conjugation (and the associated colour change) of the crosslinked polythiophenes is a result of a conformational change, and not substantially due to insertion of nitrenes. The conjugation length (in the disordered form) does not appear to have been reduced as a result of nitrene

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§This sample was crosslinked at 200 °C but no significant differences from samples crosslinked at 225 °C were seen.

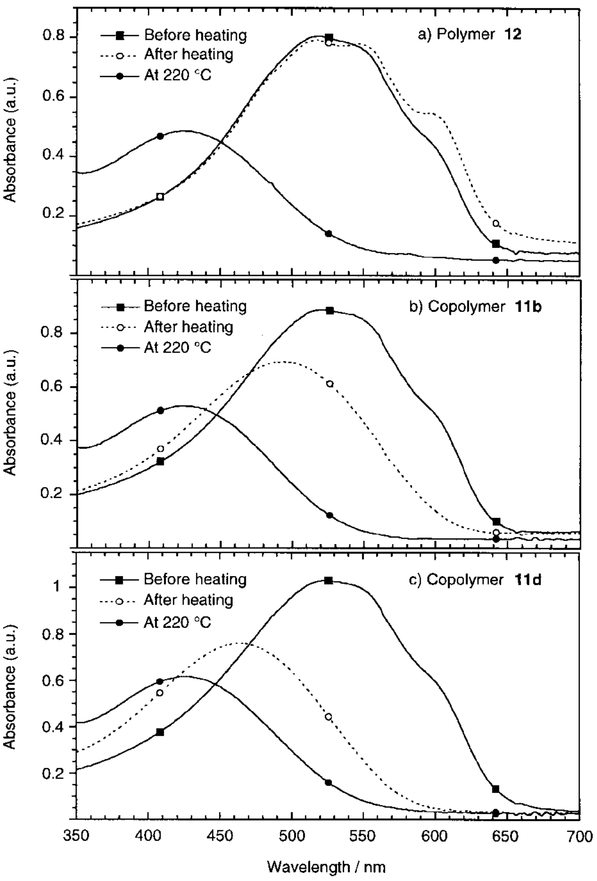

Fig. 4 Absorption spectra of polymers **12**, **11b** and **11d** (0, 9 and 25% azide side chains): before heating, after heating to 225 °C under vacuum for 30 minutes (and cooling) and then at 220 °C (in air).

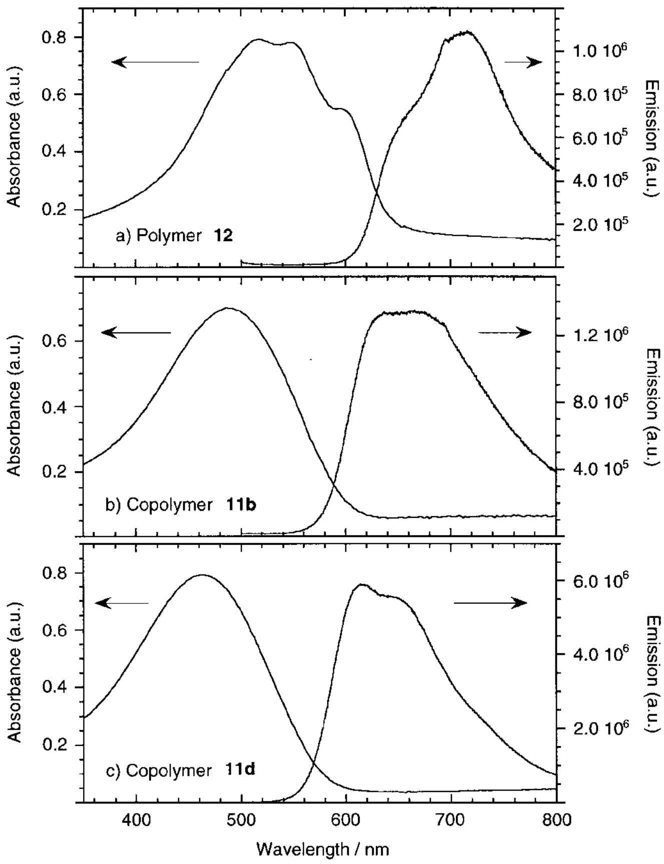

Fig. 5 Absorption spectra (left) and photoluminescence spectra (right, excitation at 480 nm) of polymers **12**, **11b** and **11d** (0, 9 and 25% azide side chains) after heating to 225 °C under vacuum for 30 minutes.

insertion, as the spectra at high temperatures are not different. The colour change on heating did not appear to be fully reversible and this indicates a slight degradation of the polymers (at high temperature in air).

Photoluminescence spectra of crosslinked films

The three films used above were also used for photoluminescence measurements (*before* heating in air). Excitation at 480 nm gave peak emission from control polymer **12** at 715 nm, from 9% azide copolymer **11b** at 630–680 nm and from 25% azide copolymer **11d** at 615 nm (Fig. 5). The three samples were of comparable thickness, and all absorb strongly at 480 nm. The emission intensity at 605 nm (6×10^6 counts s^{-1}) from copolymer **11d** (Fig. 5c) was significantly greater than that at 720 nm (1×10^6 counts s^{-1}) from regioregular poly(3-hexylthiophene) **12** (Fig. 5a). Since the absorbance for both films (normal incidence¶) is *ca.* 0.7 we conclude the emission of the copolymer **11d** is about six times greater than that of **12**. Therefore there is a shift in emission to shorter wavelengths, and stronger luminescence, as the degree of crosslinking is increased. A similar change has been observed in non-regioregular poly(3-alkylthiophene)s as the temperature is increased.[27] In the latter case, the change in emission is purely a result of a change in conformation as the polythiophene is heated. In our case the effect is closely similar and this would suggest again that the crosslinking has caused a permanent restriction of the polymer backbone to a more disordered and less conjugated conformation. The more efficient photoluminescence from the disordered (orange) conformation as compared to the ordered (purple) form is also seen in solutions of regioregular poly(3-dodecylthiophene) in toluene solution and in toluene–methanol solutions respectively.[45,46] Similarly, photoluminescence from solutions of polythiophenes in chloroform is more efficient than from solid polythiophene samples and this is thought to be due to the presence of more non-radiative decay pathways in the more crystalline and ordered solid form.[47]

Conclusions

Regioregular polythiophenes have been synthesised containing azide-substituted side chains. Thermal decomposition of these azides caused crosslinking and formation of insoluble polythiophene films. A permanent colour change was seen on crosslinking and this was interpreted as a change in conformation as a result of crosslinking at high temperature when the polythiophene backbone is in a disordered conformation. The crosslinking is assumed to create a more rigid structure which cannot then relax back to a fully ordered conformation. Those polymers with higher azide contents are the most crosslinked and therefore more restricted to a permanent disordered conformation; polymers with lower azide contents can more closely recover an ordered conformation on cooling. Some degree of control over the absorption and photoluminescence spectra of the regioregular polythiophenes was therefore possible.

The thermochromism and photoluminescence displayed by the crosslinked films **11b** and **11d**, when compared with uncrosslinked regioregular poly(3-hexylthiophene) **12**, also indicate that the colour change is due to a change in conformation rather than a disruption of conjugation as a result of nitrene insertion along the polymer backbone. However it is not possible, with these polymers and with the experiments

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¶This comparison is qualitative as the alignment of the film in the spectrometer can produce different intensities, and also it is set at grazing incidence (22°).

described, to determine the degree of nitrene insertion onto the conjugated polymer backbone (as opposed to onto other side chains). A crosslinking method which occurs at low temperature, such as a photochemical process, would not be expected to lead to a colour change, although in that case the polymer backbone might be damaged by the irradiation.

The insoluble, crosslinked polythiophenes would be suitable for incorporation into multilayer devices as further layers might be formed on top of the polythiophene by solution processing techniques. The solvation that is shown by these polymers does however indicate that a boundary between the insoluble polythiophene and additional layers might not be discrete but gradual, which would have a bearing on the performance of such devices.

Experimental

1H and ^{13}C NMR spectra were recorded on Bruker AM-200 (^1H, 200 MHz; ^{13}C, 50 MHz) and AM-500 (^1H, 500 MHz) instruments; shifts are given in units of δ relative to tetramethylsilane ($\delta = 0$ ppm); coupling constants J are given in units of Hz. Microanalyses were carried out by the staff of the University Chemical Laboratory Microanalytical Department. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. UV–Visible spectra were recorded on Hewlett Packard HP8452A diode array and Perkin Elmer Lambda 2 spectrophotometers. Solid UV samples were spun onto Spectrosil discs from solution and solution samples were held in a 1 cm cuvette with quartz windows. Photoluminescence spectra were performed on a SPEX fluoromax spectrometer using thin polymer films on Spectrosil discs, spun from 20 mg ml^{-1} solutions and heated to 225 °C under vacuum for 30 minutes. Electron-impact (EI) and chemical ionisation (CI) mass spectra were recorded by the University Chemical Laboratory Mass Spectrometry Service or the EPSRC Mass Spectrometry Service, Swansea. Gel permeation chromatography (GPC) was performed with a Polymer Laboratories PLgel 5 μ mixed-C 1 × 30 cm column and a UV–vis detector, and is calibrated against narrow distribution polystyrene standards. Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer instrument by the Department of Materials Science, Cambridge. Flash column chromatography was carried out using Merck 9385 Kieselgel 60 (230–400 mesh). All reactions were carried out under an inert atmosphere (argon or nitrogen).

3-(Undec-10-enyl)thiophene 1

A solution of 1-bromoundec-10-ene (11.1 g, 61 mmol) in dry diethyl ether (15 cm^3) was added dropwise to a stirred suspension of magnesium turnings (1.49 g, 61 mmol) in dry diethyl ether (5 cm^3) and stirred for 1 h at room temperature. The grey solution was transferred *via* a cannula to a dropping funnel and was added dropwise to a suspension of $NiCl_2(dppp)$[38] (0.11 g, 0.20 mmol, 0.45 mol%) and 3-bromothiophene (7.3 g, 45 mmol) in dry diethyl ether (15 cm^3), to maintain a gentle reflux. The solution was then stirred for 3 days at room temperature and carefully quenched with dilute HCl (1 mol dm^{-3}, 20 cm^3). The orange organic layer was washed with water (twice) and brine, dried and the solvent evaporated to give an orange liquid. Distillation (Kugelrohr, 100–130 °C, 0.1 mmHg) gave a mixture of 3-(undec-10-enyl)thiophene **1** (~96 mol%) and 3-(undec-9-enyl)thiophene **2** (~4 mol%) (5.81 g, 55%) as a colourless liquid. R_F 0.40 (hexane) (Found: C, 76.4; H, 10.5. $C_{15}H_{24}S$ requires C, 76.2; H, 10.2%); ν_{max} ($CHCl_3$)/cm^{-1} 3060w (alkene CH), 2900s, 2840s (alkane CH), 1630w (C=C), 1440 m (thiophene), 990 m and 910s ($RCH=CH_2$); δ_H of **1** (250 MHz, $CDCl_3$) 1.20–1.45 (12H, br m, 3′ to 8′-H), 1.62 (2H, br quintet, J ~7.4, 2′-H), 2.02 (2H, q, J 6.7, 9′-H), 2.62 (2H, t, J 7.7, 1′-H), 4.90–5.04 (2H, m, 11′-H), 5.82 (1H, ddt, J 17.0, 10.2 and 6.7, 10′-H), 6.93 (2H, m) and 7.23 (1H, m); δ_H due to **2** (250 MHz, $CDCl_3$) 5.38–5.44 (0.12H [2H], m, C*H*=C*H*CH$_3$), other peaks obscured by **1**; δ_C of **1** (63.5 MHz, $CDCl_3$) 29.0, 29.2, 29.4, 29.5, 29.6, 29.8, 30.3, 30.6 and 33.8 (1′ to 9′-C), 114.1 (11′-C), 119.7 (2-C), 125.0 (5-C), 128.3 (4-C), 139.2 (10′-C) and 143.2 (3-C); m/z (EI) (M^+ 236.1601; $C_{15}H_{24}S$ requires 236.1599) 236.2 (40, M), 111.0 (25), 98.0 (100) and 97.0 (60). Thiophene ^{13}C NMR assignments follow those of Bäuerle *et al.*[40]

3-(11-Hydroxyundecyl)thiophene 3 and 3-(10-hydroxyundecyl)thiophene 4

To a stirred solution of the alkenes **1** and **2** (96:4) (5.76 g, 24.3 mmol) in dry hexane (50 cm^3) at 0 °C was added, dropwise, borane–dimethyl sulfide[39] (~10 mol dm^{-3}, 0.85 cm^3, 8.5 mmol). The solution was stirred at room temperature for 2 h then cooled to 0 °C and a solution of KOH (2.2 g, 39 mmol) in water (10 cm^3) and ethanol (20 cm^3) was added dropwise, followed by aqueous H_2O_2 (100 vol., 30%, 12 cm^3, 106 mmol). The two-phase solution was vigorously stirred for 30 min at room temperature, poured into brine (200 cm^3) and extracted into ethyl acetate (3 × 150 cm^3). The combined organic fractions were dried and evaporated to dryness under reduced pressure to give a colourless solid (6.4 g). Recrystallisation from diethyl ether at 0 °C (3 crops) gave 3-(11-hydroxyundecyl)thiophene **3** (1.68 g, 27%, mp 34.0–35.5 °C) as a white solid (pure by ^1H NMR, data as below).

Careful column chromatography (hexane–ethyl acetate, 3:1) of the mother liquor, with recolumning of mixed fractions, gave further 3-(11-hydroxyundecyl)thiophene **3** (3.43 g, 55%, total 82%) as a white solid. R_F 0.34 (hexane–EtOAc, 2:1), mp 35.0–35.5 °C (Found: C, 70.75; H, 10.4; S, 12.7. $C_{15}H_{26}SO$ requires C, 70.8; H, 10.3; S, 12.6%); ν_{max} ($CHCl_3$)/cm^{-1} 3600–3300w,br (OH), 2910s, 2840s (alkane CH) and 1450 m (thiophene); δ_H (200 MHz, $CDCl_3$) 1.25–1.40 (14H, br m, 3′ to 9′-H), 1.50–1.70 (5H, m, 2′, 10′ and O-H), 2.62 (2H, t, J 7.6, 1′-H), 3.63 (2H, t, J 6.6, 11′-H), 6.92 (2H, m) and 7.23 (1H, dd, J 4.9 and 3.0); δ_C (50 MHz, $CDCl_3$) 25.7 (9′-C), 29.3–29.5 and 32.8 (1′ to 8′, 10′-C), 63.0 (11′-C), 119.7 (2-C), 125.0 (5-C), 128.2 (4-C) and 143.2 (3-C); m/z (EI) (M^+ 254.1698; $C_{15}H_{26}SO$ requires 254.1704) 254.2 (35, M), 111.0 (16), 98.0 (100) and 97.0 (50).

Column chromatography also gave 3-(10-hydroxyundecyl)thiophene **4** (0.22 g, 3.5%) as a colourless liquid (< 3% primary alcohol **3** by ^1H NMR). R_F 0.38 (hexane–EtOAc, 2:1); ν_{max} (liquid film, NaCl)/cm^{-1} 3200–3500 m,br (OH), 2925s (CH), 2855 m (CH) and 1465 m (thiophene); δ_H (500 MHz, $CDCl_3$) 1.19 (3H, d, J 6.2, 11′-H), 1.26–1.48 (15H, m, 3′ to 9′-H and OH), 1.62 (2H, quintet, J ~7.2, 2′-H), 2.62 (2H, t, J 7.7, 1′-H), 3.79 (1H, sextet, J ~6.0, 10′-H), 6.91–6.94 (2H, m) and 7.23 (1H, dd, J 4.8 and 3.0); δ_C (50 MHz, $CDCl_3$) 23.4 (11′-C), 25.7 (8′-C), 29.2–29.5, 30.2, 30.5 (1′ to 7′-C), 39.3 (9′-C), 68.1 (10′-C), 119.7 (2-C), 125.0 (5-C), 128.2 (4-C) and 143.2 (3-C); m/z (EI) (M^+ 254.17050; $C_{15}H_{26}SO$ requires 254.17044) 254.2 (28, M), 239.1 (4, $M-CH_3$), 98.0 (100) and 97.0 (60).

2-Bromo-3-(11-hydroxyundecyl)thiophene 5

To a solution of 3-(11-hydroxyundecyl)thiophene **3** (3.40 g, 13.4 mmol) in dry dimethylformamide (15 cm^3) at 0 °C and in the dark was added, dropwise, a solution of *N*-bromosuccinimide (2.40 g, 13.5 mmol) in dry dimethylformamide (25 cm^3).[40] The solution was allowed to warm to room temperature and was stirred for 4 h, poured into water–brine (1:1, 200 cm^3) and extracted into EtOAc (4 × 75 cm^3). The EtOAc fractions were washed with brine, dried and the solvent removed under reduced pressure to give a pale yellow liquid. Flash chromatography with hexane–EtOAc (2:1) eluent gave the monobrominated alcohol **5** (4.32 g, 97%) as a colourless liquid. R_F 0.30 (hexane–EtOAc, 2:1) (Found: C, 54.1; H, 7.6; S, 9.7; Br, 23.9. $C_{15}H_{25}SOBr$ requires C, 54.05; H, 7.6; S, 9.6; Br, 24.0%); ν_{max} (CCl_4)/cm^{-1} 3635 m, 3350–3500 m,br (OH), 2915s, 2860s (alkane CH), 1465 m, 1410 m and 1050s (C–O); δ_H (200 MHz, $CDCl_3$) 1.17–1.62 (19H, m, 2′ to 10′-H, OH), 2.56 (2H, t, *J* 7.6, 1′-H), 3.59–3.69 (2H, m, 11′-H), 6.79 (1H, d, *J* 5.7, 4-H) and 7.18 (1H, d, *J* 5.6, 5-H); δ_H (200 MHz, C_6D_6) 1.20–1.60 (18H, m, 2′ to 10′-H), 2.51 (2H, t, *J* 7.5, 1′-H), 3.40 (2H, t, *J* 6.0, 11′-H), 6.51 (1H, d, *J* 5.7, 4-H) and 6.69 (1H, d, *J* 5.6, 5-H); δ_C (50 MHz, $CDCl_3$) 25.7 (9′-C), 29.2–29.5 (1′ to 8′-C), 32.8 (10′-C), 63.1 (11′-C), 108.8 (2-C), 125.1 (5-C), 128.2 (4-C) and 141.9 (3-C); *m/z* (CI) (MNH_4^+ 350.1153; $C_{15}H_{29}N^{79}BrOS$ requires 350.1153); 352, 350 (100, 98, MNH_4) and 253 (26, M − Br).

2-Bromo-3-[11-(2-tetrahydropyranyloxy)undecyl]thiophene 6

To a solution of 2-bromo-3-(11-hydroxyundecyl)thiophene **5** (4.28 g, 12.8 mmol) in dry dichloromethane (35 cm^3) was added toluene-*p*-sulfonic acid (82 mg, 0.48 mmol) and 3,4-dihydro-2*H*-pyran (1.5 g, 18 mmol). The solution rapidly turned violet and, more slowly, olive. The solution was stirred for 20 h at room temperature and washed with water and brine, dried and the solvent removed under reduced pressure to give a brown liquid. Flash chromatography with dichloromethane–hexane (1:1) eluent gave the protected alcohol **6** (4.78 g, 89%) as a colourless liquid. R_F 0.40 (CH_2Cl_2) (Found: C, 57.6; H, 7.8; S, 7.5; Br, 19.0. $C_{20}H_{33}SO_2Br$ requires C, 57.5; H, 8.0; S, 7.7; Br, 19.1%); ν_{max} (liquid film, NaCl)/cm^{-1} 2935s, 2855s (alkane CH), 1465 m, 1410w, 1350 m and 1035s (C–O); δ_H (200 MHz, $CDCl_3$) 1.20–1.45 (14H, br s, 3′ to 9′-H), 1.45–1.89 (10H, m, 2′, 10′ and 3″ to 5″-H), 2.55 (2H, t, *J* 7.6, 1′-H), 3.38 (1H, dt, *J* 9.6 and 6.6, 11′-H), 3.44–3.55 (1H, m, 6″-H), 3.73 (1H, dt, *J* 9.6 and 6.8, 11′-H), 3.82–3.93 (1H, m, 6″-H), 4.57 (1H, m, 2″-H), 6.79 (1H, d, *J* 5.7, 4-H) and 7.18 (1H, d, *J* 5.5, 5-H); δ_H (200 MHz, C_6D_6) 1.20–1.93 (24H, m, 2′ to 10′ and 3″ to 5″-H), 2.51 (2H, t, *J* 7.5, 1′-H), 3.37–3.53 (2H, m, 11′ and 6″-H), 3.83–4.00 (2H, m, 11′ and 6″-H), 4.67 (1H, dd, *J* 3.4 and 3.4, 2″-H), 6.51 (1H, d, *J* 5.6, 4-H) and 6.69 (1H, d, *J* 5.6, 5-H); δ_C (50 MHz, $CDCl_3$) 19.7 (4″-C), 25.5, 26.2, 29.2–29.7 and 30.8 (1′ to 10′, 3″ and 5″-C), 62.3 and 67.7 (11′ and 6″-C), 98.8 (2″-C), 108.8 (2-C), 125.1 (5-C), 128.2 (4-C) and 142.0 (3-C); *m/z* (CI) (MNH_4^+ 434.1728; $C_{20}H_{37}N^{79}BrO_2S$ requires 434.1729) 436, 434 (3, 3, MNH_4), 352, 350 (4, 4, MNH_4− THP group), 337 (2, M − Br), 102 (100, $C_5H_{10}O_2$) and 85 (60, C_5H_9O).

3-Hexylthiophene 7

3-Hexylthiophene **7** was synthesised according to the published procedure.[41]

2-Bromo-3-hexylthiophene 8

Following Bäuerle,[40] 3-hexylthiophene **7** (16.1 g, 96 mmol) was mono-brominated with *N*-bromosuccinimide (17.5 g, 98 mmol) in dry dimethylformamide (100 cm^3) at 0 °C. Distillation of the crude product (80 °C, 0.2 mmHg) gave 2-bromo-3-hexylthiophene **8** (18.5 g, 78%) as a colourless liquid. R_F 0.50 (hexane); δ_H (200 MHz, $CDCl_3$) 0.88 (3H, t, *J* 6.5, 6′-H), 1.25–1.37 (6H, m, 3′ to 5′-H), 1.49–1.64 (2H, m, 2′-H), 2.56 (2H, t, *J* 7.6, 1′-H), 6.79 (1H, d, *J* 5.6, 4-H) and 7.18 (1H, d, *J* 5.7, 5-H); δ_H (200 MHz, C_6D_6) 0.89 (3H, t, *J* 6.4, 6′-H), 1.16–1.35 (6H, m, 3′ to 5′-H), 1.47 (2H, br quintet, *J* ~7, 2′-H), 2.48 (2H, t, *J* 7.6, 1′-H), 6.49 (1H, d, *J* 5.6, 4-H) and 6.68 (1H, d, *J* 5.7, 5-H). These data are in accord with those previously reported.[14]

Copolymerisations and copolymer reactions

The syntheses of copolymers **9a–d**, **10a–d** and **11a–d** are illustrated using the 9:1 copolymer series, **9b**, **10b** and **11b**.

Regioregular 9:1 poly{3-hexylthiophene-*co*-3-[11-(2-tetrahydropyranyloxy)undecyl]thiophene} 9b. Following the procedure of McCullough,[14,19] a mixture of 2-bromo-3-hexylthiophene **8** (1.47 g, 5.95 mmol) and 2-bromo-3-[11-(2-tetrahydropyranyloxy)undecyl]thiophene **6** (0.28 g, 0.67 mmol) was copolymerised with a single addition of $NiCl_2$(dppp) and a reaction time of 66 h to give the copolymer **9b** (108 mg, 9%) as a deep purple solid film (insoluble in hexane and soluble in chloroform). λ_{max} ($CHCl_3$)/nm 450; δ_H (200 MHz, $CDCl_3$) 0.91 (t, *J* 6.4, 6′-H [3H] of hexyl), 1.20–1.80 (br m, side chain CH_2), 2.81 (2H, br t, *J* 7.6, 1′-H), 3.31–3.54 (0.2H, m, 11′, 6′-H [2H] of THPO-undecyl), 3.66–3.90 (0.2H, m, 11′, 6′-H [2H] of THPO-undecyl), 4.57 (0.1H, m, 2″-H [1H] of THPO-undecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 9500, M_w 13 400, polydispersity 1.42.

Regioregular 9:1 poly[3-hexylthiophene-*co*-3-(11-hydroxyundecyl)thiophene] 10b. A solution of the copolymer **9b** (107 mg, ~0.58 mmol, 0.06 mmol of OTHP) in chloroform (2.5 cm^3) was added to methanol (12 cm^3) to give a deep purple suspension. Dilute aqueous HCl (2 mol dm^{-3}, 1.5 cm^3) was added and the suspension was stirred at reflux for 16 h and allowed to cool. The precipitate was collected by centrifuge and washed twice with methanol, washed into a flask with chloroform and evaporated to dryness under reduced pressure to give the 9:1 11-hydroxyundecyl:hexyl copolymer **10b** (95 mg, 93%) as a deep purple solid. λ_{max} (solid)/nm 526, 550sh and 600sh, ($CHCl_3$)/nm 450; δ_H (200 MHz, $CDCl_3$) 0.91 (br t, *J* ~6.4, 6′-H [3H] of hexyl), 1.20–1.80 (br m, side chain CH_2), 2.81 (2H, br t, *J* ~7.5, 1′-H), 3.62 (0.2H, t, *J* 6.5, 11′-H [2H] of 11-hydroxyundecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 11 500, M_w 19 000, polydispersity 1.65.

Regioregular 9:1 poly[3-hexylthiophene-*co*-3-(11-azidoundecyl)thiophene] 11b. To a solution of regioregular 9:1 poly[3-hexylthiophene-*co*-3-(11-hydroxyundecyl)thiophene] **10b** (77 mg, ~0.043 mmol OH) in dry THF (2 cm^3) was added triphenylphosphine (46 mg, 0.175 mmol), di-*tert*-butyl azodicarboxylate (43 mg, 0.187 mmol) and diphenylphosphoryl azide (39 ml, 0.181 mmol).[42,48] The red solution was stirred at room temperature and in the dark for 5 days and the THF was then evaporated (with a stream of nitrogen). The resultant purple solid was dissolved in chloroform (1.5 cm^3) and added to methanol (10 cm^3). The purple suspension which formed was stirred for 0.5 h and the solid was isolated by centrifuge, washed with methanol, acetone and methanol, transferred to a flask with chloroform and evaporated to dryness to give the azidated copolymer **11b** (63 mg, 81%) as a deep purple solid film. ν_{max} (KBr disc)/cm^{-1} includes 2095w (azide); λ_{max} (solid/nm) 522, 550sh and 600sh, ($CHCl_3$/nm) 450; δ_H (200 MHz, $CDCl_3$) 0.91 (br t, *J* ~6.7, 6′-H [3H] of hexyl), 1.20–1.80 (br m, side chain CH_2), 2.81 (2H, br t, *J* ~7.4, 1′-H), 3.23 (0.16H, t, *J* ~7, 11′-H [2H] of 11-azidoundecyl) and 6.98 (1H, s, 4-H); GPC ($CHCl_3$, 450 nm)/Da M_n 12 900, M_w 23 300, polydispersity 1.80; DSC: exotherm at 185 °C, max. at 200 °C (not seen on second sweep—nitrene formation and reaction).

Summary of GPC data for all other copolymers

9a M_n 10 400, M_w 15 500; **10a** M_n 11 800, M_w 19 600; **11a** M_n 11 400, M_w 21 200; **9c** M_n 11 300, M_w 15 800; **10c** M_n 14 000, M_w 32 700; **11c** M_n 16 900, M_w 60 600; **9d** M_n 12 800, M_w 21 200; **10d** M_n 9800, M_w 24 700; **11d** M_n 14200, M_w 143 700.

Regioregular poly(3-hexylthiophene) 12

This polymer was prepared from 2-bromo-3-hexylthiophene **8** following the procedure of McCullough.[14]

Thermal crosslinking experiments

Thin polymer films for UV–visible spectra were spun onto Spectrosil discs from chloroform solution ($\sim$15 mg ml^{-1}). Thin films for infrared spectra were free-cast onto freshly pressed blank KBr discs, from chloroform solution ($\sim$15 mg ml^{-1}). Crosslinking experiments were carried out in a drying pistol at 0.1 mmHg at 225 °C for 30 minutes. The drying pistol was allowed to cool to room temperature before the samples were removed.

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