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Synthesis and polymerisation of α,ω-bis(3-pyrrolyl)alkanes

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Abstract—The synthesis, characterisation and polymerisation studies of a homologous series of α,ω-bis(pyrrolyl)alkanes are described. These α,ω-bis(pyrrolyl)alkanes were produced using Friedel–Crafts acylation followed by reduction of the carbonyl group using Red-Al®. Chemical polymerisation of the resultant dimers using $FeCl_3$ produced poly(α,ω-bis(pyrrolyl)alkane) films, which were characterised by SEM, FTIR and tested for conductivity.

1. Introduction

The cross-linking of polymers has proven to increase the strength, brittleness, rigidity or even the elasticity of the resultant polymers. For example, one of the first processes to form cross-linked polymers was the addition of sulfur during the vulcanisation of rubber, which produces a harder, more robust form of rubber.[1]

The cross-coupling of two pyrrole molecules for the purpose of forming conductive polymers can occur at the nitrogen, C-2 or C-3 positions. Previous work has shown that the introduction of an alkyl chain to couple two heterocyclic molecules at the C-2 position alters a variety of properties, such as flexibility and elasticity.[1–4] Aromatic spacers have also been used for this purpose and upon polymerisation of such dimers large changes in conductivity and solubility were noted.[5,6] Various pyrrole dimers have previously been synthesised by coupling at the C-2 positions, these dimers have been used for multiple applications, the major use being for sensor technologies.[7–11]

Generally, polymers that possess a high degree of cross-linking require a monomer that has three or more sites for polymerisation and this is usually achieved by first synthesising a dimer. For thiophene and pyrrole this is generally achieved by the fixation of a linker from the C-3 position. Pyrrole dimers can also be produced easily by cross-linking through the nitrogen.[12–22] However, for our future applications of these polymers, the nitrogen position must be unfunctionalised as it is involved in fixation to specific substrates.[23]

There has been a large number of publications on cross-linked monomers of thiophene linked through the C-3 position such as α,ω-bis(thienyl)alkanes (Fig. 1). These α,ω-bis(thienyl)alkane molecules when polymerised are reported to have good conductivity and are highly flexible.[24–32] In contrast, studies on the cross-coupling of pyrrole at the C-3,3′-positions are scarce and the published work has been limited to theoretical studies, patent examples or synthesis for specific purposes.[33–35]

Detailed herein are the synthesis, polymerisation and characterisation of a dimer family of α,ω-bis(pyrrolyl)alkanes. The ideal structure of α,ω-bis(pyrrolyl)ethane (Fig. 2) illustrates the high degree of cross-linking, the extent of which

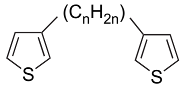

Figure 1. α,ω-Bis(thienyl)alkanes.

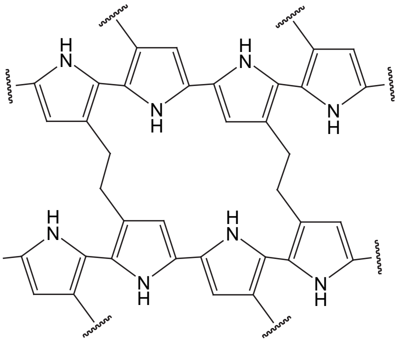

Figure 2. Ideal polymer structure for poly(1,2-bis(pyrrolyl)ethane).

Keywords: Conducting polymers; Cross-linked polymers; Cross-coupled pyrrole; Pyrrole dimers; Pyrrole.

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can be reduced by the introduction of another monomer unit during polymerisation, i.e., synthesis of copolymers.

2. Results and discussion

A four-step process was employed for the synthesis of the pyrrole dimers (Scheme 1). Initially, pyrrole was protected with a tosyl group, then Friedel–Crafts acylation of the tosyl-protected pyrrole provided high yields of the 3-acylated product. Removal of the protecting group was achieved under basic conditions and finally, Red-Al® reduction yielded the desired α,ω-bis(pyrrolyl)alkanes.

Due to its ability to deactivate the C-2 and C-5 positions and activate the C-3 and C-4 positions of pyrrole, the tosyl protecting group for the N-1 position on pyrrole was chosen. For the acylation reaction the shorter carbon chain diacid dichlorides were more reactive and required inert conditions (dry N_2 gas) in order to obtain a reasonable yield. The longer chain diacid dichlorides were more stable, allowing the reaction to be completed without strict anhydrous conditions and good yields were obtained. Purification by column chromatography gave the desired products, with the yield generally increasing as the chain length increased (Table 1, Fig. 3).

Removal of the protecting group involved refluxing a dimer (**2a**–**2i**) in 1,4-dioxane with NaOH (5 M in water) overnight. For the larger alkyl chain derivatives (**3f**–**3i**) purification by recrystallisation in a petroleum spirits/methanol mixture gave the product in high yields (Table 1). For the shorter alkyl chain derivatives (**3a**–**3e**) purification proved to be more difficult, with column chromatography required. Unfortunately the shortest chains, n=0 (**3a**) and n=2 (**3b**), polymerised readily in the presence of air and light, with little un-polymerised product left after the overnight reflux.

The final step in the synthesis of the α,ω-bis(pyrrolyl)-alkanes was the reduction of the carbonyl group. This was achieved using Red-Al® solution under inert conditions. Once again for the two shortest linkers (**4a** and **4b**) poor yields were obtained. The reduction of the deactivating carbonyl group afforded unstable dimers that underwent instantaneous polymerisation. The rest of the dimers (**4c**–**4i**) were more stable, resulting in high yields (Table 1) of the desired compounds after purification using column chromatography.

Table 1. Isolated yields for the α,ω-bis(*N*-tosyl pyrrolyl)alkanoyl compounds

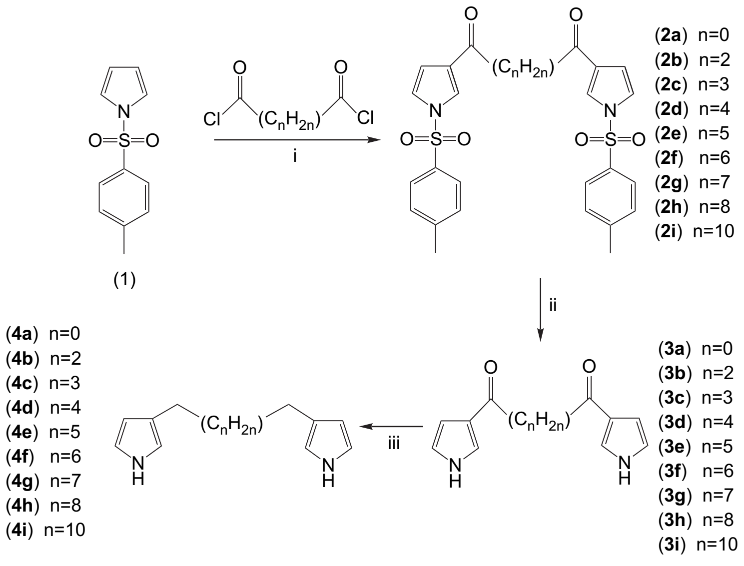
Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**
n	0	2	3	4	5	6	7	8	10
Yield (%)	22	42	52	68	74	92	91	95	93
Compound	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**
n	0	2	3	4	5	6	7	8	10
Yield (%)	12	14	76	37	43	83	98	96	98
Compound	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**	**4i**
n	0	2	3	4	5	6	7	8	10
Yield (%)	41[a]	55[a]	91	80	88	90	91	96	91

[a] Yield of a black insoluble polymeric material.

The polymerisation of the dimers **4a**–**4i** was achieved by oxidation with $FeCl_3$ (Scheme 2). The conditions for polymerisation were varied for different purposes. For formation of polymers **5a**–**5i** as powders stirring of a specific dimer **4a**–**4i** in solution (water or organic solvents) was followed by the addition of $FeCl_3$. If the polymerisation was performed at low temperatures with rapid stirring very fine powders were produced.

Polymer films were produced by polymerisation of the dimers using the minimum amount of solvent in a wide recrystallisation dish. The dimer and oxidising agent were mixed quickly in solvent and the solvent was allowed to evaporate providing thin films that were simply peeled off the glassware. The resultant thin films were very flexible (Fig. 4), however, as the thickness of the film increased the flexibility decreased.

The films that were produced were investigated by SEM for surface characteristics. The films that were cast using water produced a homogeneous surface as shown in Figure 5. The films that were produced from the evaporation of chloroform



Scheme 1. Synthesis of α,ω-bis(pyrrolyl)alkanes (**4a**–**4i**). (i) $AlCl_3$, 0 °C, CH_2Cl_2, 4 h; (ii) NaOH, reflux, 1,4-dioxane, 14 h; (iii) Red-Al®, 0 °C, THF, 3 h.

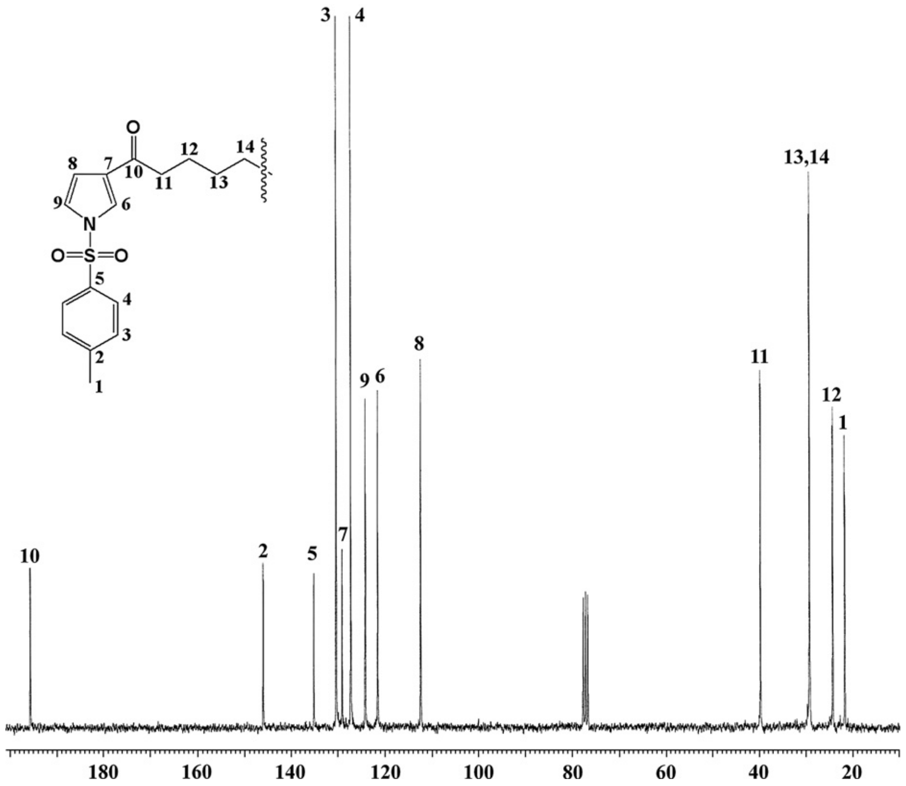
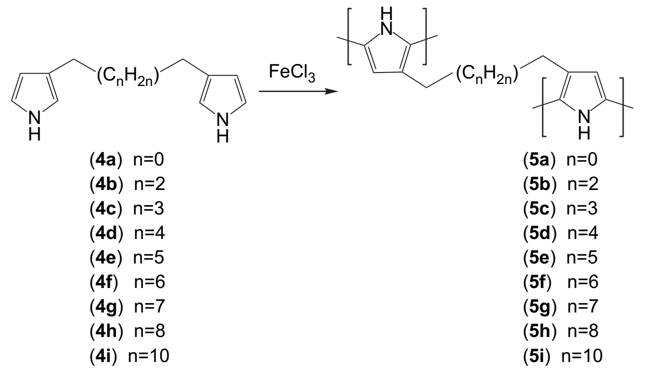


Figure 3. ^{13}C NMR of 1,10-bis(*N*-tosyl-3-pyrrole)decane-1,10-dione (**2h**).



Scheme 2. Polymerisation of α,ω-bis(pyrrolyl)alkanes (**4a**–**4i**).

exhibited a 'bubbled' effect (Fig. 6), which has been seen before with poly(3-alkylpyrroles).[23,36]

The poly(1,10-bis(pyrrolyl)decane) films formed by the evaporation of water were more brittle than those formed by evaporation of chloroform, this was possible due to encapsulated chloroform in the polymer matrix (Fig. 5). The crack on the right side of the image is characteristic of these films, whereas the films formed by the evaporation of chloroform did not exhibit this brittleness.

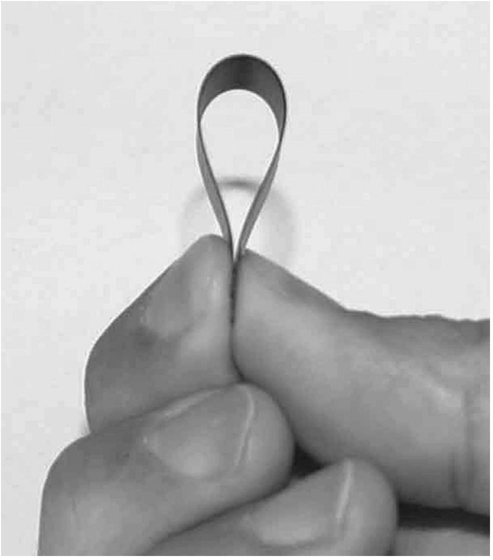


Figure 4. Flexibility of poly(1,10-bis(pyrrolyl)decane) films (**5h**).

The poly(α,ω-bis(pyrrolyl)alkane) samples were prepared for conductivity measurements by two different methods. The growth of thin conductive films by solution polymerisation and subsequent evaporation of solvent was the first method tried, the other was the grinding and compression of the poly(α,ω-bis(pyrrolyl)alkane) powders formed from solution polymerisation into disks. The thin polymer films exhibited higher conductivity due to their continuous surfaces; therefore, these films were used throughout the conductivity tests.

Unlike the poly(3-alkylpyrroles), for which a steady decrease in conductivity was observed as the alkyl chain length increased,[36] the poly(α,ω-bis(pyrrolyl)alkane) films showed no obvious trends. Two conductivity maxima were observed when 5-carbon (**5c**) and 8-carbon (**5f**) alkyl chain couplers are used (Fig. 7) with the latter possessing the highest conductivity.

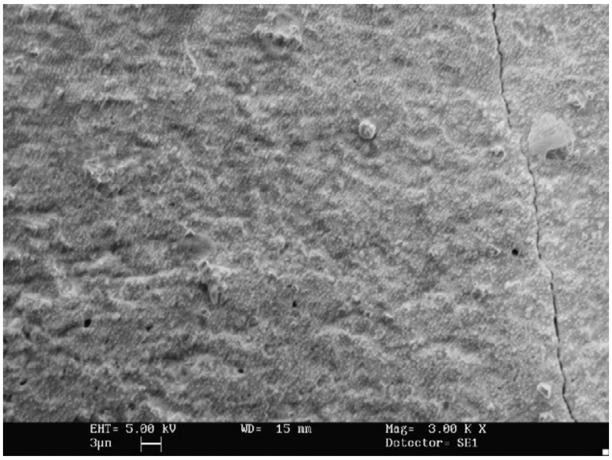


Figure 5. Scanning electron micrograph of 1,10-bis(pyrrolyl)decane polymerised with $FeCl_3$ in a minimum amount of water, which was subsequently evaporated. Magnification 3000×.

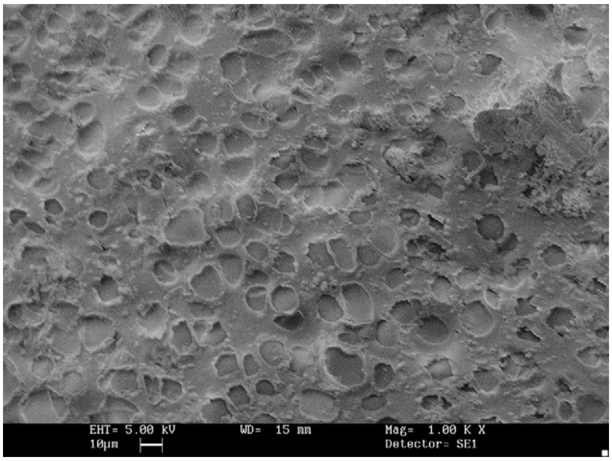


Figure 6. Scanning electron micrograph of 1,10-bis(pyrrolyl)decane polymerised with $FeCl_3$ in a minimum amount of chloroform, which was subsequently evaporated. Magnification 1000×.

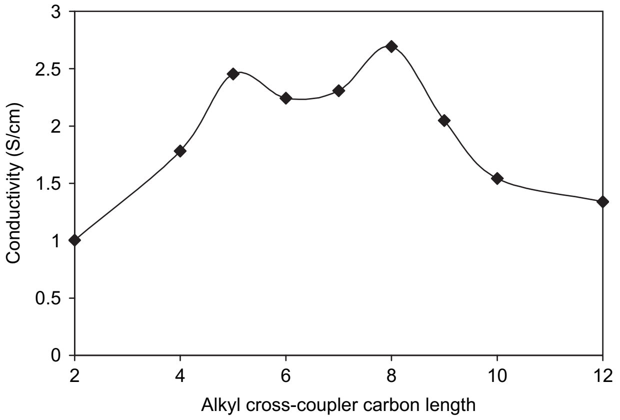


Figure 7. Conductivity of films produced from the solution polymerisation of α,ω-bis(pyrrolyl)alkanes.

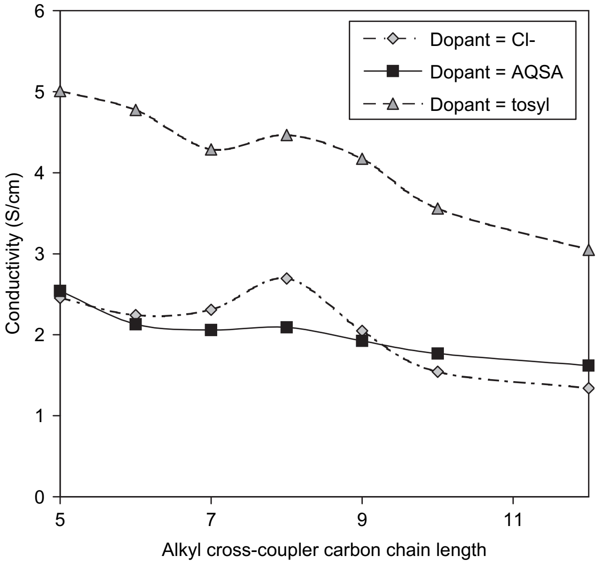


Figure 8. Conductivity testing of films produced by solution polymerisation in the presence of Cl^-, AQSA and tosyl dopants.

Polymers formed from controlled polymerisations using $FeCl_3$ have a higher conductivity due to the $FeCl_3$ acting as a source of Cl^- as a dopant, thus decreasing the band gap and promoting the movement of electrons along the polymer chains.[37] The use of other dopants was also investigated, the results of which can be seen in Figure 8. Due to the light and temperature sensitivity of the dimers **4a** and **4b** they polymerised uncontrollably to produce polymers **5a** and **5b**, and as these polymers were not produced under controlled conditions they were not tested for dopant effects.

Three different dopants were used, namely Cl^- (from $FeCl_3$), anthraquinone-2-sulfonic acid sodium salt (AQSA) and tosyl sodium salt. The results obtained from the AQSA and $FeCl_3$ were approximately the same, with the only difference being that the AQSA dopant produced polymers that had a more uniform decrease in conductivity with increase in alkyl chain length. A marked improvement in conductivity resulted from the use of the tosyl dopant, which showed approximately double the reported conductivity of the polymers formed in the presence of the Cl^- or AQSA dopants. In general the trend for these polymers is a decrease in conductivity as the cross-coupling carbon chain length is increased. However, it is interesting to note that there is a divergence in this trend for the poly(1,8-bis(pyrrolyl)octane) (**5f**) films with respect to all three dopants tested.

Assessing all experimental data and the results from conductivity tests it was determined that eight carbons was the optimum chain length. Three factors led to this conclusion: a high percentage yield, greater stability of the longer alkyl chain dimers and the conductivity could be greatly increased with a judicious choice of dopant.

In conclusion the synthesis of the α,ω-bis(pyrrolyl)alkanes was achieved in relatively high yields, however, the synthesis of shorter cross-coupled carbon chain lengths (n=0–2) of α,ω-bis(pyrrolyl)alkanes was difficult. Due to air and light sensitivity, these shorter chain dimers polymerised uncontrollably. Stability of the larger chain α,ω-bis(pyrrolyl)-alkanes (n>7) allowed isolated yields in excess of 95% to be accomplished.

The solution polymerisation method produced highly flexible conductive films when solvent evaporation from $CHCl_3$ was employed. Modifying polymerisation parameters allowed the resultant polymer to be forged in different solid states such as powders. The optimum monomer for yield and conductivity was poly(1,8-bis(pyrrolyl)octane). The conductivity of the poly(α,ω-bis(pyrrolyl)alkanes) can be improved by the appropriate choice of dopants. The AQSA dopant had little effect, however, the tosyl sodium salt caused a substantial increase in the observed conductivity.

3. Experimental section

3.1. Materials and methods

All chemicals were purchased from Sigma–Aldrich (>98% purity) and used as supplied. THF was distilled from sodium/benzophenone ketyl under dry nitrogen. CH_2Cl_2 was distilled from CaH_2 and stored over 4 Å molecular sieves.[38] Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{256} aluminium backed plates, which were developed in a chromatotank. Visualisation was achieved using a UV lamp or by an oxidising dip comprised of K_2CO_3 (1.0 g), $KMnO_4$ (1.0 g) and H_2O (100 mL). TLC plates were dipped, then dried using a heat gun to ensure that all compounds became visible. Column chromatography was performed using silica gel (60–270 mesh). Solution state NMR spectra were recorded using a Jeol JNM-GX 270 MHz or a JNM-ECP 400 MHz spectrometer as indicated and referenced against tetramethylsilane (TMS).[39] Two-dimensional (2D) NMR spectra (COSY, HMQC and HMBC) were recorded on the JNM-ECP 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million and coupling constants are reported in hertz. Melting points were measured on a Reichart hot-stage microscope and are uncorrected. Scanning electron microscope (SEM) images were recorded on a Leica S440 Scanning Electron Microscope. The samples were prepared by sputter coating a thin layer of gold (~7–10 nm) onto the textile surface. New compounds were characterised using elemental analysis (Chemical and Micro Analytical Services Pty. Ltd. Belmont, Victoria, Australia). Solid pellets of polymer were formed by grinding the polymer and pressing into disks. Four probe conductivity measurements were performed on the solid disks or films using a Fluke multimeter.

3.1.1. *N-p*-Toluenesulfonylpyrrole (1). A solution of pyrrole (25.00 g, 0.37 mol), KOH (41.85 g, 0.75 mmol) and tosyl chloride (66.73 g, 0.35 mol) in THF (1.10 L) was prepared. The solution was refluxed for 4 h, cooled to rt, whereupon diethyl ether (500 mL) was added and the reaction mixture transferred to a separatory funnel. The reaction mixture was washed with copious amounts of water (5×250 mL) followed by a saturated NaCl solution (3×250 mL). The organic layer was separated, dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The resulting grey solid was recrystallised from methanol (200 mL) to yield the desired product as a fine white powder (73.70 g, 90%); mp 100–102 °C; δ_H (270 MHz, $CDCl_3$) 2.38 (3H, s, CH_3), 6.26 (2H, t, *J* 2.2 Hz, Py), 7.14 (2H, t, *J* 2.0 Hz, Py), 7.26 (2H, d, *J* 9.4 Hz, tosyl), 7.74 (2H, d, *J* 8.4 Hz, tosyl); δ_C (67.9 MHz, $CDCl_3$) 21.7, 113.6, 120.8, 126.9, 130.1, 136.1, 145.1.[40]

3.1.2. Synthesis of the α,ω-bis(*N*-tosyl-3-pyrrolyl)alkanoyl compounds (2a–2i). The appropriate alkyl diacid chloride (0.9 mol equiv) in dry CH_2Cl_2 (20 mL/g) was added to a solution of $AlCl_3$ (2.0 mol equiv) in dry CH_2Cl_2 (20 mL/g of $AlCl_3$) in one portion at rt under a nitrogen atmosphere. After 10 min the reaction was cooled to 0 °C and a solution of *N*-tosyl-pyrrole (**1**) (2.0 mol equiv) in CH_2Cl_2 (10 mL/g) was added dropwise over 5 min. This was stirred at 0 °C for 2 h before ice water was added cautiously and the product extracted using diethyl ether (3×200 mL). The organic portions were combined, dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The resultant products were purified using column chromatography with petroleum spirits/ethyl acetate (3:2) as the eluent. Products isolated were white/grey solids or clear oils (22–93%). All yields, ^1H and ^{13}C NMR and elemental data are located in the Supplementary data.

3.1.3. Synthesis of the α,ω-bis(3-pyrrolyl)alkanoyl compounds (3a–3i). An NaOH solution in water (5 M, 100 mL/g of the dimer **2a**–**2i**) was added to a cross-coupled tosyl-protected pyrrole (one of **2a**–**2i**) dissolved in 1,4-dioxane (100 mL/g of **2a**–**2i**) and the mixture refluxed overnight. The mixture was cooled and extracted with diethyl ether (3×100 mL). The organics were combined, dried (Na_2SO_4) and the solvent removed under reduced pressure. The resultant products **3a**–**3c** were purified using column chromatography with petroleum spirits/ethyl acetate (3:2) as the eluent, yielding oils (12–76%), or recrystallised using petroleum spirits for the larger products (**3d**–**3i**) yielding white powders (37–98%). All yields, ^1H and ^{13}C NMR and elemental data are located in the Supplementary data.

3.1.4. Synthesis of α,ω-bis(pyrrolyl)alkanes (4a–4i). Under an atmosphere of nitrogen **3a**–**3i** (31.00 mmol) was dissolved in THF (125 mL) and cooled to 0 °C while stirring. A solution of Red-Al® (65% w/w, in toluene, 19.95 g, 64.00 mmol) was added slowly. The solution was allowed to warm to rt and stirring continued for 3 h. After heating the reaction mixture at 50 °C for 1 h, the solution was cooled to 0 °C and cautiously hydrolysed by the slow addition of water (100 mL). The crude product was extracted with diethyl ether (3×50 mL) and dried (Na_2SO_4). The solvent was removed and the product distilled at 0.01 mmHg to yield a dark oil, or recrystallised from hexane/dichloromethane (1:1) to yield a white powder (41–96%). All ^1H and ^{13}C NMR for **4c**–**4i** are located in the Supplementary data, **4a** and **4b** polymerised immediately and could not be measured.

3.1.5. Synthesis of poly(α,ω-bis(3-pyrrolyl)alkanes) (5c–5i).

3.1.5.1. Method A. A dimer (one of **4c**–**4i**) (5.0 mmol) was stirred in $CHCl_3$ (100 mL) while $FeCl_3$ (5.0 mmol) was added in one portion and the reaction left stirring for 3 h. The reaction mixture was filtered to separate the black polymer, which was ground into a powder and washed with copious amount of water to remove iron impurities. The polymer powder was placed under reduced pressure (0.1 mmHg) for 4 h before being processed into thin disks for conductivity measurements. The disks produced were extremely brittle making the conductivity measurements difficult.

3.1.5.2. Method B. A flat dish with a large surface area (200×200 mm) was filled with solvent (water or chloroform) to a depth of 2 mm. A dimer (one of **4c–4i**) (5.0 mmol) and $FeCl_3$ (5.0 mmol) were added and the reaction mixture was left, allowing the solvent to evaporate. This occurred over varying lengths of time depending on the solvent used. The resultant polymer film was soaked in water followed by an aqueous HCl solution at pH 2. The film was dried under reduced pressure (0.1 mmHg) for 4 h before being tested for conductivity. The films that were produced were flexible making conductivity measurements possible.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.010.

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