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Synthesis and Properties of Two Regular Thienylpyrrole Polymers

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ABSTRACT: Two examples of polymers containing both thiophene and pyrrole units have been synthesized via a one-pot organometallic Stille reaction. The physical, thermal, and electronic properties of these polymers have been investigated: They have band gaps at about 2.4 eV and conductivities as high as 1.28×10^{-1} S/cm (iodine-doped) and 2.30×10^{-3} S/cm (undoped).

Introduction

Polythiophene and polypyrrole have been widely investigated as potential materials in the field of molecular electronics. These polymers are insoluble and intractable and therefore not easily processable for real applications.[1] Polypyrrole in its neutral reduced state is also highly reactive toward oxygen, due to its negative oxidation potential (−0.2 V vs SCE).[2] As a result, polypyrrole is not a good candidate in applications involving redox cycling. Polythiophene, on the other hand, has a rather high oxidation potential (0.7 V vs SCE)[3] and can be reduced by a variety of reagents without decomposition. However, a relatively high potential is required to cyclize the material between the doped and undoped states. The preparation of hybrid polymers containing both thiophene and pyrrole units provides an attractive approach to tailored electroactive materials, with the added advantage of incorporating solubilizing groups on the pyrrole nitrogen, thus providing a route to processable polymers. In addition to engineered electronic properties, some copolymers have also been reported to protect semiconductor surfaces from photocorrosion.[4] Copolymers of thiophene and pyrrole have so far been obtained only by anodic or chemical oxidation of structured thienylpyrrole oligomers[5−15] or by the electrochemical oxidation of pyrrole mixed with thiophene oligomers.[4,16−19] However, these methods can produce polymers with significant branching and an irregular distribution of the monomeric units. Different known organometallic methodologies have been employed to obtain heterocyclic polymers of well-defined conjugated architectures and enhanced electronic properties.[20−24] The Stille carbon−carbon bond formation reaction has been extensively used in synthetic organic chemistry due to its regiospecifity, as well as its tolerance toward a wide variety of functional groups on the coupling partners.[25] Moreover, unlike other organometallic coupling components, the organotin compounds are not particularly oxygen or moisture sensitive. The Stille coupling reaction between an organic halide and an organostannane has recently been applied to the synthesis of regular polypyrroles and hybrid polymers containing thiophene and phenylene units.[26,27] The versatility of the Stille reaction is utilized in this paper to prepare two well-ordered thiophene and pyrrole-containing copolymers, the thermal and electrical properties of which are reported.

Results and Discussion

The two new thienylpyrrole copolymers investigated in this study, shown in Figure 1, have a terthienyl-*N*-dodecylpyrrole (polymer **1**) and a quaterthienyl-*N*-dodecylpyrrole (polymer **2**) repeat unit, respectively. The long aliphatic substitutent on the pyrrolic nitrogen was incorporated with the object of increasing the polymer solubility.

The key intermediate used in the preparation of the thienylpyrrole copolymers was dithienyl-*N*-dodecylpyrrole (**3**). The synthesis and purification of the terheterocycle **3** has been reported by us recently in three steps starting from 2-acetylthiophene.[28] Dilithiation of **3** with 2 mol of nBuLi/TMEDA in THF medium, followed by a DMF quench and subsequent hydrolysis, afforded in 76% yield the known 5,5′-disubstituted dicarboxaldehyde.[28] The selectivity of the dilithiation at the free α-positions was utilized in a one-pot Stille coupling reaction (Scheme 1) to obtain the desired polymers. Employing the same metalation procedure, the distannyl derivative **4** was prepared by the dilithiation of **3**, followed by quenching with tributyltin chloride. The resulting distannyl intermediate **4** was not isolated in pure form, since attempted silica chromatography caused extensive destannylation. However, it was generated from **3** using a *10% excess* of nBuLi followed by a *10% excess* of tributyltin chloride, a procedure which was used to ensure complete distannylation. The solution of **4** was then syringed into a solution containing $Pd(PPh_3)_4$[29] and a 10% excess of the dibromo compound **5** or **6**. An excess of dibromide was employed deliberately, with the double objectives of producing major amounts of soluble lower molecular weight polymers with the bromine end group detectable by analysis.

The reaction mixture was refluxed for 3 days, and the resulting polymer was precipitated by dilution with methanol. After washing with water to remove any inorganics, any excess tin reagent and lower oligomers were removed by Soxhlet extraction of the resultant orange-red powder with acetone. Further Soxhlet extraction with 1,2-dichloroethane (DCE) followed by THF gave different polymer fractions. The DCE fraction formed the major amount in the case of both polymers **1** and **2**, and it alone was extensively investigated further for its physical, thermal, and electroactive

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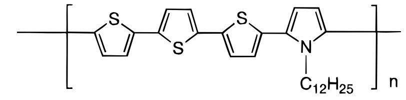

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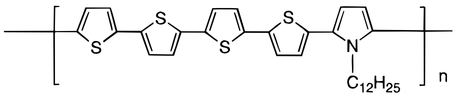

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Figure 1. Structures of the thienylpyrrole containing copolymers.

Scheme 1. One-pot Synthesis of Thienylpyrrole Polymers 1 and 2

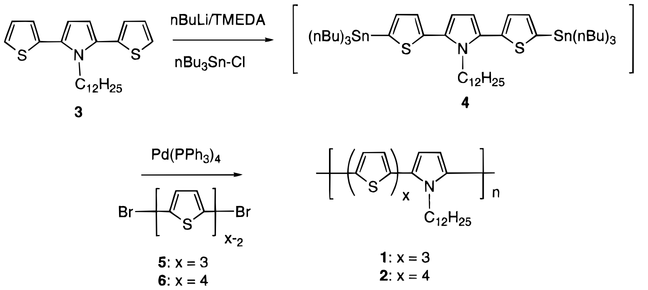


Table 1. Molecular Weights of the Copolymers by GPC Measurements

thienylpyrrole polymer	fraction	M_w	PDI (M_w/M_n)	M_n	no. of repeat units (n)	no. of heterocyclic units
1	DCE	1.23×10^4	1.18	1.04×10^4	~22	~88
	THF	1.71×10^4	1.30	1.32×10^4	~28	~112
2	DCE	5.42×10^3	1.24	4.37×10^3	~8	~40
	THF	7.57×10^3	1.19	6.36×10^3	~11	~55

Table 2. Molecular Weights of the Copolymers by End Group Analysis

thienylpyrrole polymer	fraction	% Br	mol wt	no. of repeat units (n)	no. of heterocyclic units
1	DCE	6.16	2.60×10^3	~5	~20
	THF	3.91	4.09×10^3	~8	~32
2	DCE	9.08	1.76×10^3	~2–3	~13
	THF	8.31	1.93×10^3	~3	~15

properties. The polymers were soluble in a number of organic solvents, such as DCE, $CHCl_3$, chlorobenzene, and THF. The molecular weights of the different fractions were determined by GPC measurements on a Shimadzu gel permeation chromatograph equipped with a UV detector using THF as solvent (flow rate = 1 mL/min). Four Hibar Lichrogel columns (EM Industries) were used in series with pore sizes of 10^5, 10^4, 10^3, and 10^2 Å. Polystyrene calibration standards were used for plotting the calibration curve. From the obtained values of weight average molecular weights (M_w) and polydispersity indices (PDI), the number average molecular weights (M_n) were calculated. The GPC results are summarized in Table 1.

An alternate molecular weight estimation was calculated by end group bromine analysis. Since an excess of the dibromo component was used in the coupling reactions, it is reasonable to assume bromo end groups in the thienylpyrrole polymers **1** and **2**. The results are shown in Table 2.

From the number of repeat units n, obtained by end group analysis, the percentages of C, H, N, and S were back-calculated, and the values showed a close match to those obtained from elemental analysis. End group molecular weight determination results of the polymers reveal low molecular weights for the polymers. The molecular weights by end group analysis were considerably lower than those obtained by GPC measurements (Table 1). The inflated values of the molecular weights obtained by GPC could be attributed to the rigid rod nature of the polymeric backbone. The GPC measurements give an estimate of the hydrodynamic volume, and thus the coiled polystyrene standards used for the GPC measurements may lead to erroneous results in the case of rigid rod polymers. Lower molecular weights are obtained in the case of polymer **2** in comparison to **1**, due to the lower ratio of solubilizing *N*-dodecylpyrrole units in the polymer. The lower molecular weight of **2** correlates with a lower value of the wavelength of the UV–vis absorption maximum (λ_{max} in chloroform): DCE fraction = 437 nm; THF fraction = 443 nm compared with **1** (λ_{max} in chloroform): DCE fraction = 442 nm; THF fraction = 453 nm.

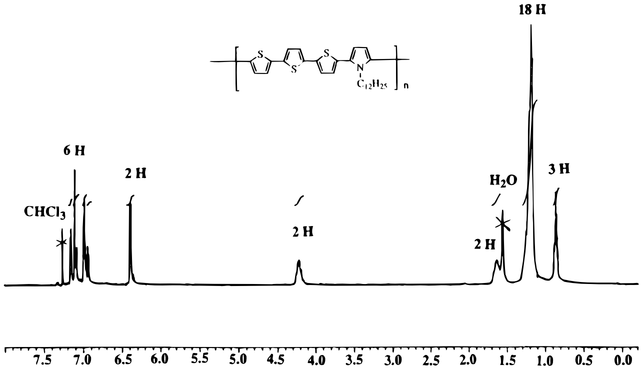


Figure 2. ^{1}H NMR of thienylpyrrole polymer **1**.

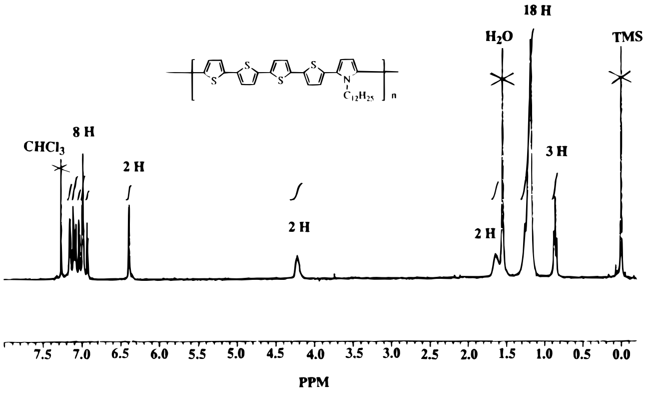


Figure 3. ^{1}H NMR of thienylpyrrole polymer **2**.

From the proton NMR of the two polymers (DCE fraction), shown in Figures 2 and 3, the thienyl ring protons appear as multiplets between 6.8 and 7.2 ppm. The protons of the N-dodecyl side chains resonate at ca. 0.86 ppm ($-C\mathbf{H}_3$), 1.11–1.26 ppm ($-(C\mathbf{H}_2)_9CH_3$), 1.64 ppm ($NCH_2C\mathbf{H}_2-$), and 4.22 ppm ($NC\mathbf{H}_2-$). The pyrrole protons appear as doublets at around 6.38 ppm, suggesting appreciable rotational barriers in the polymers. This is further substantiated by the complexity of the thiophene resonances in the aromatic region of the proton NMR spectra. Rotational isomers possible for polymer **1** are shown in Figure 4.

Thermal Behavior of the Polymers (DCE Fractions). The differential scanning calorimetry (DSC) measurements of polymers **1** and **2** (Figures 5 and 6), carried out under N_2 at a heating rate of 5 °C/min, showed glass transition temperatures (T_g) of ~52 and

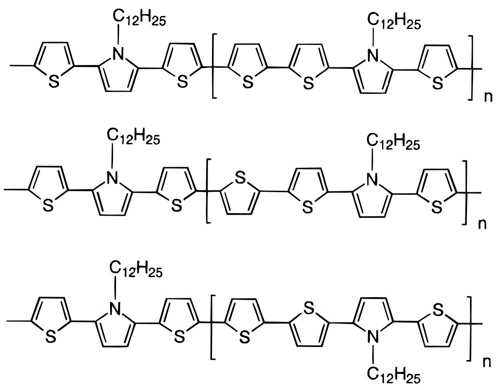


Figure 4. Possible rotational isomers for polymer **1**.

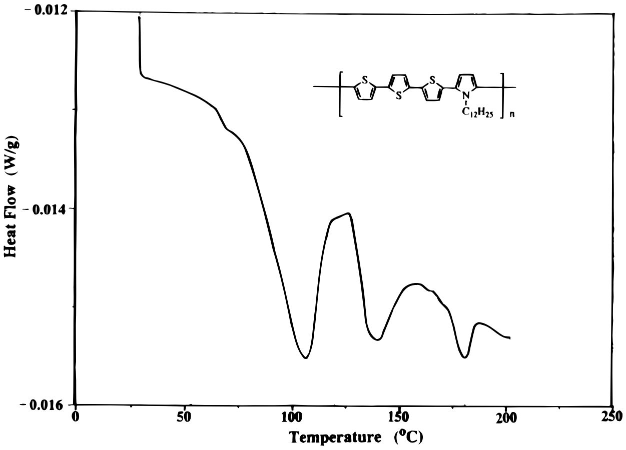


Figure 5. DSC thermogram of thienylpyrrole polymer **1**.

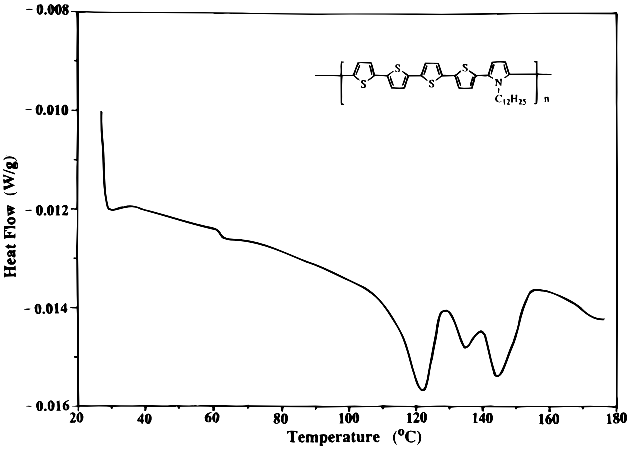


Figure 6. DSC thermogram of thienylpyrrole polymer **2**.

54 °C, respectively. The low glass transition temperatures can be attributed to the presence of long flexible dodecyl chains on the pyrrolic units in the rigid polymer backbone. For polymer **1** (Figure 5), three additional endotherms were observed at 106, 140, and 180 °C. The different melting points could be explained by the presence of several components of different molecular weights or by the presence of different polymer phases. The DSC of the lower molecular weight polymer **2** (Figure 6) displayed melting points at 121, 134, and 144 °C. The thermal stability of the polymers was studied by thermogravimetric analysis (TGA) under N_2 at a heating rate of 20 °C/min. The TGA measurements of the polymers are depicted in Figures 7 and 8. The high molecular weight polymer **1**, containing terthienylpyrrole repeat units, showed a 3% weight loss at 260 °C and a 20% weight loss at 475 °C. The low molecular weight polymer **2**, containing quaterthienylpyrrole repeat units, underwent a 3% weight loss at 250 °C and a 20% weight loss at 450 °C.

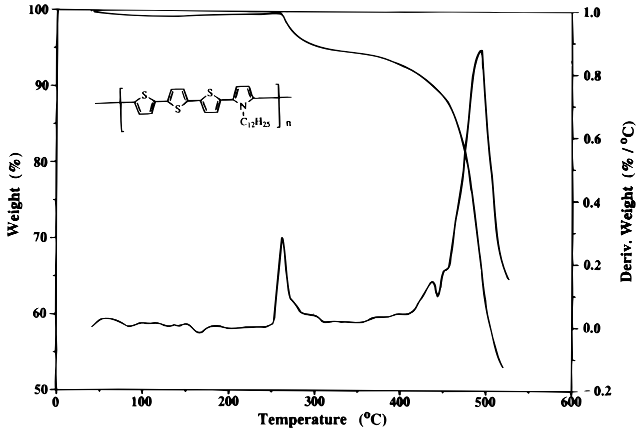


Figure 7. TGA thermogram and first derivative plot of thienylpyrrole polymer **1**.

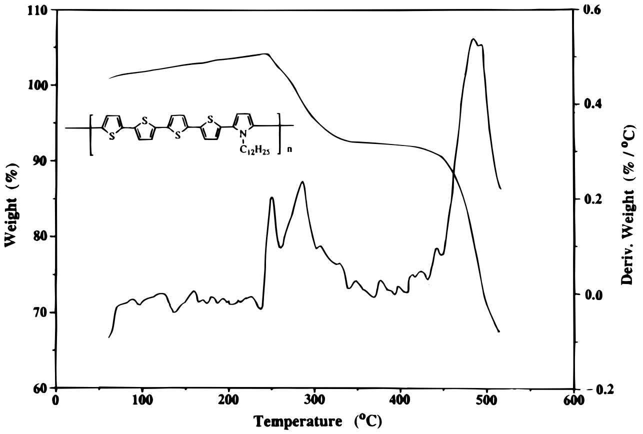


Figure 8. TGA thermogram and first derivative plot of thienylpyrrole polymer **2**.

Electrochemistry and Electronic Properties of the Copolymers (DCE Fractions). The oxidation potentials of the polymers were measured by cyclic voltammetry at two different scan rates (100 and 500 mV/s) in a 0.1 M solution of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) in DCE. A single compartment cell with a Pt disk was used as the working electrode, with a Pt wire as an auxiliary electrode, and potentials were measured (vs SCE reference) using a PAR EG&G M263 potentiostat. The terthienyl-1-dodecylpyrrole system **1** showed one broad reversible redox wave with an oxidation potential of 0.57 V (Figure 9). Interestingly, the low molecular weight quaterthienyl-*N*-dodecylpyrrole system **2** displayed two broad redox waves (Figure 10), with a first oxidation potential at 0.64 V and the second at 0.98 V. This higher first oxidation potential in the case of polymer **2** can be rationalized as due to the greater number of the less easily oxidized thiophene rings in each repeat unit; a similar situation has been observed by us in the case of lower thienylpyrrole oligomers.[30] As anticipated, the first oxidation potentials of the mixed polymers lie between those for polypyrrole[2] (−0.2 V) and polythiophene[3] (0.7 V).

In a further study of their electronic properties, thin films of both polymers **1**, $(SSSN)_x$ and **2**, $(SSSSN)_x$, were obtained by either the casting or the spin-coating method. Figure 11 shows the film surface structures observed by SEM. Films prepared by the spin-coating

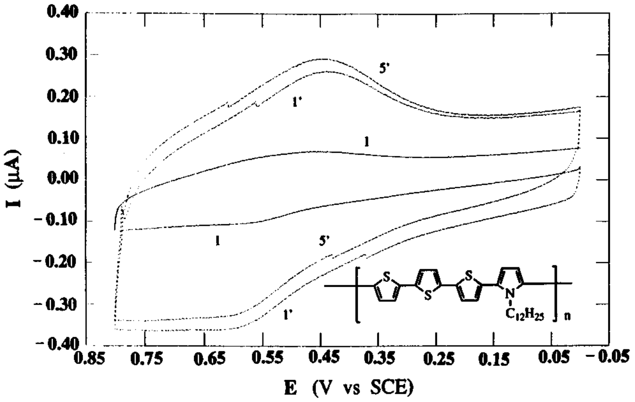


Figure 9. Cyclic voltammograms of thienylpyrrole polymer **1**: (1) first scan (100 mV/s); (1′) first scan; (5′) fifth scan (500 mV/s).

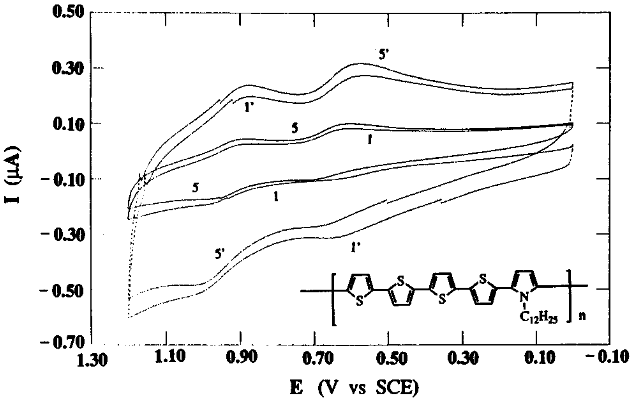
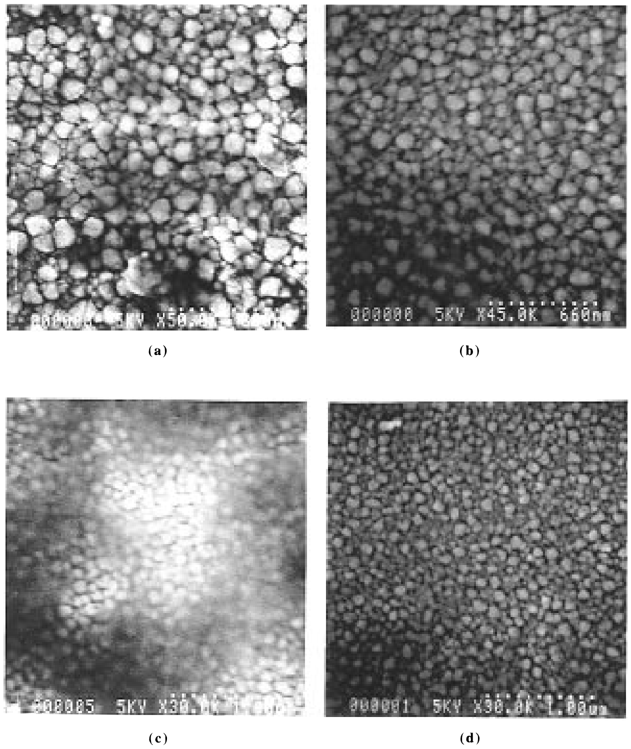


Figure 10. Cyclic voltammograms of thienylpyrrole polymer **2**: (1) first scan; (5) fifth scan (100 mV/s); (1′) first scan; (5′) fifth scan (500 mV/s).

method did not present any apparent irregularities and their surfaces were quite smooth, whereas films obtained by the casting route presented a rough surface. From the SEM morphology, it is obvious that the spin-coating method gave better quality films with a much more homogeneous surface, as compared to the casting method. Figure 12 shows a typical plot of doping time against conductivity for $(SSSN)_x$ and $(SSSSN)_x$ thin films doped with iodine. To our surprise, both polymers in the neutral undoped state (dark red in color) already exhibited conductivities in the semiconductor range, with $\sigma = 2.30 \times 10^{-3}$ S cm^{-1} for polymer **1**, $(SSSN)_x$, and $\sigma = 2.26 \times 10^{-5}$ S cm^{-1} for polymer **2**, $(SSSSN)_x$. The conductivities for thin films of both $(SSSN)_x$ and $(SSSSN)_x$ doped with iodine grew rapidly in the first 43 min, from 2.26×10^{-3} to 1.07×10^{-1} S/cm for $(SSSN)_x$ and 2.45×10^{-5} to 5.6×10^{-3} S/cm for $(SSSSN)_x$. After the sharp increase, the conductivities of both films gradually reached a maximum value 1.28×10^{-1} S/cm for $(SSSN)_x$ and 1.92×10^{-2} S/cm for $(SSSSN)_x$. During doping, the color of the films changed from brown or yellow-brown to almost black. Exposing the thin films to air resulted in a decrease in the conductivities of the mixed polymers. After 24 h, the conductivity values dropped to 7.76×10^{-3} S/cm for $(SSSN)_x$ and 1.16×10^{-4} S/cm for $(SSSSN)_x$.

These data are summarized in Table 3. In both the undoped and doped state, the electrical conductivity is higher for **1**, $(SSSN)_x$, than for **2**, $(SSSSN)_x$.



(a) (b)

(c) (d)

Figure 11. SEM micrographs of $(SSSN)_x$ and $(SSSSN)_x$ thin films deposited on an ITO glass substrate by casting and spin-coating: (a) $(SSSN)_x$ cast film; (b) $(SSSN)_x$ spin-coated film; (c) $(SSSSN)_x$ cast film; (d) $(SSSSN)_x$ spin-coated film.

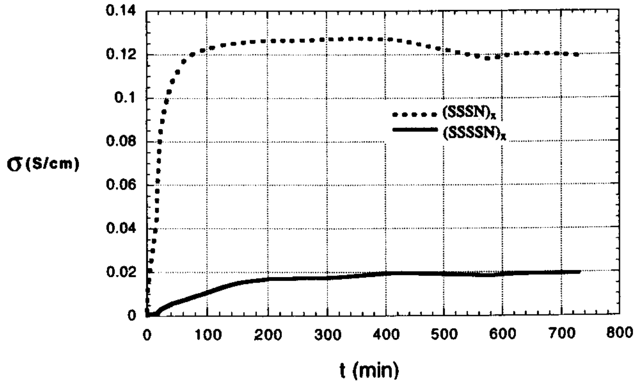


Figure 12. Plot of doping time vs room-temperature conductivity for $(SSSN)_x$ and $(SSSSN)_x$ thin films doped with iodine.

Table 3. Physical Properties of Polymers 1, $(SSSN)_x$, and 2, $(SSSSN)_x$

	1, $(SSSN)_x$	**2**, $(SSSSN)_x$
molar mass/Da	2.6×10^3 (DCE)	1.76×10^3 (DCE)
conductivity, undoped/S cm^{-1}	2.30×10^{-3}	2.26×10^{-5}
conductivity, I_2-doped/S cm^{-1}	1.28×10^{-1}	1.92×10^{-2}
E_3/eV	E_F(Au)-7.0	E_F(Au)-8.1
E_2/eV	E_F(Au)-4.1	E_F(Au)-4.6
E_1/eV	E_F(Au)-2.0	E_F(Au)-2.3
E_g(VUV)/eV	2.4	2.4

UPS spectra are shown in Figures 13 and 14 for solution-cast films of **1** and **2**, respectively. The UPS binding energies E_b are measured relative to the Fermi level [E_F(Au)] of the Au substrate; E_F(Au) is 3.72 eV below the vacuum level (Figure 14). These spectra can be compared to those of polythiophene and of several oligothiophenes reported by Fujimoto et al.[31] The main feature, at $E_3 = 7.0$ eV (**1**) and 8.1 eV (**2**), corresponds to similar features between $E_b = 6$ and 8 eV for the oligothiophenes, which are from several occupied molecular orbitals lower in energy than the HOMO. The shoulders at $E_2 = 4.1$ eV (**1**) and 4.6 eV (**2**) may

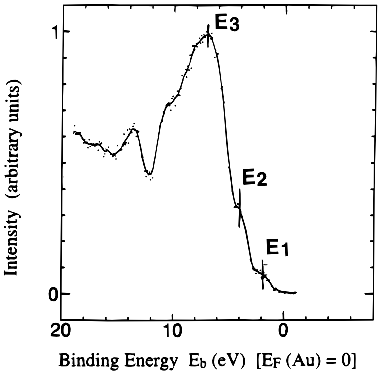


Figure 13. Ultraviolet photoelectron spectrum of a cast film of polymer **1**, $(SSSN)_x$, on Au [intensity (arbitrary units) vs binding energy E_b (eV), relative to Fermi level E_F of the Au substrate (whose work function is 3.72 eV)]. Three energy levels are indicated.

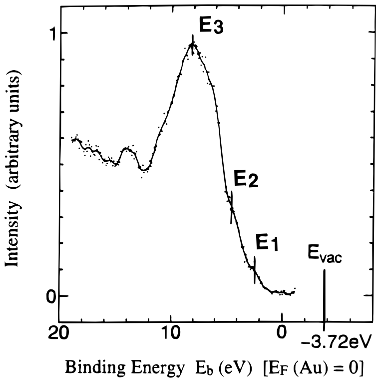


Figure 14. Ultraviolet photoelectron spectrum of a cast film of polymer **2**, $(SSSSN)_x$, on Au [intensity (arbitrary units) vs binding evergy E_b (eV), relative to Fermi level E_F of the Au substrate (whose work function is 3.72 eV)]. Three energy levels are indicated.

correspond to the nonbonding occupied orbital found at $E_b = 3.5$ eV for all longer oligothiophenes S_n, for $n \geq 5$,[31] but for the thiophene–pyrrole polymers of this study the spectrum is, comparatively, not as well resolved (Figures 13 and 14). The small shoulders at $E_1 = 2.0$ eV (**1**) and 2.6 eV (**2**) are close to similar features in polythiophene and poly(2-methylthiophene).[31] From the visible absorption edges band gaps $E_g = 2.4$ eV are estimated for both polymers. These gaps lie between those reported for polythiophene[3] (2.2 eV) and polypyrrole[2] (2.5 eV).

In conclusion, a simple one-pot organometallic procedure has been devised for the preparation of two well-defined hybrid polymers containing thiophene and *N*-dodecylpyrrole units. Low molecular weight polymers were obtained, which were soluble in a number of common organic solvents. These polymers showed reasonable thermal stability and tailored electroactive properties.

Experimental Section

Physical Characterization. The polymer thin films of the DCE fractions of both **1**, $(SSSN)_x$, and **2**, $(SSSSN)_x$, were prepared by both casting and spin-coating techniques. For doping and conductivity measurements, $(SSSN)_x$ or $(SSSSN)_x$ powder samples were dissolved in dichloromethane and cast into thin films. Microslide glasses coated with gold electrodes were used as substrates, and these were slowly dipped into the $(SSSN)_x$ or $(SSSSN)_x$ solutions. After 24 h, brown and yellow-brown thin films were obtained for $(SSSN)_x$ and $(SSSSN)_x$, respectively. For scanning electron microscopy (SEM) studies, thin films were prepared by both the casting and the spin-coating method. Indium tin oxide (ITO) conducting glass was used as the substrate in both cases. For the ultraviolet photoelectron spectroscopy (UPS) study, thin films of $(SSSN)_x$ or $(SSSSN)_x$ were prepared on a gold-coated glass substrate at room temperature in air by either the casting or the spin-coating method, respectively. The SEM study of film surface morphology was performed by means of a HITACHI S-900 operated at 5 kV. The thickness of these films was measured by ellipsometry (Rudolph Auto-EL-III, with a He–Ne laser, $\lambda = 632.8$ nm). The real (n) and complex (k) parts of the index of refraction of the glass microscope slide substrate were measured as $n_s = 1.414$, $k_s = 0.01$. For the thin films, a k value of zero was assumed. Iodine doping was carried out at room temperature. Thin films of polymers **1**, $(SSSN)_x$, and **2**, $(SSSSN)_x$, coated on microslide glass substrates with gold electrodes were put into a small desiccator protected from light and charged with ground iodine powder. Conductivities were measured by a standard two-probe method using a gold wire and gold paste as electrical contacts. A Hewlett Packard 3457A Multimeter was used to measure the resistances of these thin films simultaneously during the iodine doping process. The UPS system used in this study was constructed at the UVSOR Facility of the Institute for Molecular Science. Synchrotron radiation was monochromatized by a plane-grating monochromator supplying radiation in the energy range of 2–150 eV.[31,32] The Fermi energy of the UPS system was determined by using the Fermi edge of gold films evaporated *in situ*.[31,32] The thermal analyses of the polymers were performed on a DuPont 910 instrument.

General Procedure of Polymerization. To a solution of triheterocycle **3** (1.5 g, 3.76 mmol) in 20 mL of dry THF containing TMEDA (1.25 mL, 8.27 mmol) was added dropwise 2.2 M nBuLi in hexanes (3.76 mL, 8.27 mmol) at 0 °C under N_2. The mixture was stirred at 0 °C for 30 min, followed by stirring at room temperature for 10 min. To the green solution was added dropwise tributyltin chloride (2.24 mL, 8.27 mmol) at −78 °C. The reaction mixture was raised to room temperature and stirred for 1 h. The resultant golden yellow solution was transferred to a dry three-necked flask containing 2,5-dibromothiophene (**5**) (0.55 mL, 8.27 mmol) and $Pd(PPh_3)_4$[29] (0.43 g, 0.38 mmol) in 5 mL of THF at 0 °C under N_2. After refluxing for 3 days (N_2), the reaction mixture was poured into a large amount of methanol, affording a bright orange-red precipitate. Filtration and washing with water and then acetone was followed by Soxhlet extraction of the resultant solid with acetone to remove lower molecular weight oligomers. The higher molecular weight fractions were obtained by Soxhlet extraction of the insoluble orange-red solid with 1,2-dichloroethane (DCE) and then with THF. Evaporation of the extracts separately gave 0.72 g (40%) and 40 mg (2%), respectively, of the fractions of polymer **1** as red powders. The yields reported are based on the polymer repeat unit. The same procedure was adopted to obtain polymer **2** by using dibromide **6** instead of **5**. Performing the reaction on a 1.0 g scale afforded 0.97 g (69%) of the DCE polymer fraction and 60 mg (4%) of the THF polymer fraction as red powders. The major polymer fraction in the case of both polymers **1** and **2** was the DCE extract. Anal. Found for polymer **1**: (DCE extract) C, 65.00, H 6.35, Br 6.16, N 2.60, S 19.86; (THF extract) C 67.13, H 6.49, Br 3.91, N 2.74, S 19.06. Anal. Found for polymer **2**: (DCE extract) C 60.94, H 5.33, Br 9.08, N 2.05, S 22.07; (THF extract) C 61.54, H 5.62, Br 8.31, N 2.00, S 22.27.

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