Poly(alkyl thiophene-3-carboxylates). Synthesis and Characterization of Polythiophenes with a Carbonyl Group Directly Attached to the Ring

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ABSTRACT: Polythiophenes with electron-withdrawing ester groups attached at the 3-position, namely poly(hexyl thiophene-3-carboxylate) (**1a**) and poly(octyl thiophene-3-carboxylate) (**1b**), have been synthesized using the Ullmann reaction with copper powder in DMF. Characterization of the polymers includes IR, ^{1}H and ^{13}C NMR, and UV–vis spectroscopy as well as TGA and molecular weight studies. The polymers also show red-orange and red fluorescence, respectively. The same polymers prepared using Ni(0) instead of Cu gave polymer with comparable molecular weights but higher polydispersity, which was not as uniform as shown by NMR spectroscopy and which had shorter conjugation lengths, as shown by blue-shifted UV–vis absorption and fluorescence maxima.

Introduction

Polythiophenes have been the subject of intense study the past several years since they show many interesting electronic and optical properties. The syntheses of these systems typically involve oxidative polymerization or organometallic coupling reactions, and thus most of the reported polythiophenes contain either alkyl group side chains or electron-donating substituents. There currently exists no general synthesis of polythiophenes with a carbonyl group (or other strongly electron-withdrawing substituent) directly attached to the 3-position of the thiophene ring, and as a result, there is an overwhelming need for a general synthesis of these systems. There have been a few reports of attempts to electrochemically prepare polythiophenes with electron-withdrawing substituents directly attached to the thiophene ring, but the results were negative, presumably because the electron-withdrawing groups decreased the reactivity of the thiophene ring.[1,2] A few systems such as poly((fluoromethyl)- and (difluoromethyl)thiophenes) have been reported[3] and, as these compounds illustrate, the electron-withdrawing groups are generally substituted on an alkyl group attached to the thiophene ring. We now report on the preparation of poly(alkyl thiophene-3-carboxylates) (**1**) using the Ullmann coupling reaction of a dihalide and copper powder, along with the characterization of these systems. The Ullmann reaction is particularly useful for the synthesis of polythiophenes containing a large variety of strongly electron-withdrawing groups since it is well-known that such groups are completely compatible with the Ullmann reaction conditions and indeed they generally *enhance* the reaction.[4–8]

Experimental Section

General Procedures. NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$. TMS (δ = 0.00 ppm) and $^{13}CDCl_3$ (δ = 77.00 ppm) were used as internal references for ^{1}H and ^{13}C spectra, respectively. FTIR spectra were recorded either as a liquid film between NaCl plates or, for solids, as a mixture with KBr powder in a diffuse reflectance cell. Gas chromatography was done with a DB-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm coating) using a flame ionization detector. HPLC was performed using an Econosil C_{18} 10U (10 μm) reversed-phase column (250 mm × 4.6 mm) and a UV detector at 254 nm. Gel permeation chromatography (GPC) was carried out with 10^3, 10^4, and 10^5 Å Ultrastyragel columns in series, a UV detector at 254 nm, and polystyrene standards using THF solutions. All solvents were purified and dried prior to use according to standard procedures.[9]

2,5-Dibromothiophene-3-carboxylic Acid (4).[10] Thiophene-3-carboxylic acid (**3**) (2.56 g, 0.0200 mol) and 50 mL of glacial acetic acid were put into a 100 mL three-necked flask equipped with a stirring bar, a condenser, and an addition funnel. Then, 5.3 mL (0.100 mol) of Br_2 was added to the flask drop by drop at room temperature. The mixture was warmed and stirred at 60 °C for 8 h. After the reaction was complete, the mixture was poured into 200 mL of cold water (ice bath) and some Na_2SO_3 was added to decolorize. The mixture was filtered, and a light yellow solid was obtained. The crude product was recrystallized from 600 mL of EtOH–H_2O (1:2) to give 4.8 g (84%) of product **4** as needles: mp 177–179 °C (lit.[10] 175–176 °C). ^{1}H NMR: δ 10.88 (s), 7.41 (s). ^{13}C NMR: δ 165.3, 132.0, 130.8, 121.4, 111.7. Anal. Calcd for $C_5H_2O_2Br_2S$: C, 21.00; H, 0.71. Found: C, 21.20; H, 0.43.

Alkyl 2,5-Dibromothiophene-3-carboxylate (2), General Procedure. 2,5-Dibromothiophene-3-carboxylic acid (**4**) (2.9 g, 0.010 mol) and 25 mL of $SOCl_2$ were refluxed for 6 h, and the excess $SOCl_2$ was removed under vacuum. A light yellow low-melting solid was obtained. Then, 0.10 mol of *n*-ROH and 2 mL of dry pyridine were added to the flask dropwise through an addition funnel. The mixture was stirred for 6 h at 80 °C, cooled, poured into a mixture of 15 g of ice and 20 mL of 1 M HCl, and stirred. The solution was washed with ether (4 × 50 mL), and the organic phase was washed with saturated $NaHCO_3$ (3 × 50 mL) and dried (K_2CO_3). The ether was removed with a rotary evaporator, and a light yellow crude product (**2a** or **b**) was obtained and purified as described below.

Hexyl 2,5-Dibromothiophene-3-carboxylate (2a). The crude product was distilled under vacuum to give 3.11 g (84%) of product as a pale yellow liquid: bp 135–140 °C/0.05 Torr; purity (HPLC) >99.5%. ^{1}H NMR: δ 7.34 (s, 1 H), 4.27 (t, 2 H, J = 7 Hz), 1.73 (p, 2 H, J = 7 Hz), 1.3–1.5 (m, 6H), 0.90 (t, 3 H, J = 7 Hz). ^{13}C NMR: δ 160.9, 132.0, 131.7, 118.9, 111.3, 65.4, 31.4, 28.5, 25.7, 22.5, 14.0. IR: 3102, 2955, 2928, 2858, 1726, 1526, 1465, 1426, 1353, 1335, 1222, 1148, 1038, 1011, 982, 843, 770, 727 cm^{-1}. UV–vis (THF): λ_{max} 230 nm (ϵ = 7200), 273 (ϵ = 6200), 250 (sh), 265 (sh). Anal. Calcd for $C_{11}H_{14}O_2Br_2S$: C, 35.70; H, 3.81. Found: C, 35.95; H, 3.73.

Octyl 2,5-Dibromothiophene-3-carboxylate (2b). The crude product was distilled under vacuum to give 3.23 g (81%) of product as a low-melting pale yellow solid: mp 41–42 °C; purity (HPLC) >99.5%. ^{1}H NMR: δ 7.35 (s, 1 H), 4.27 (t, 2

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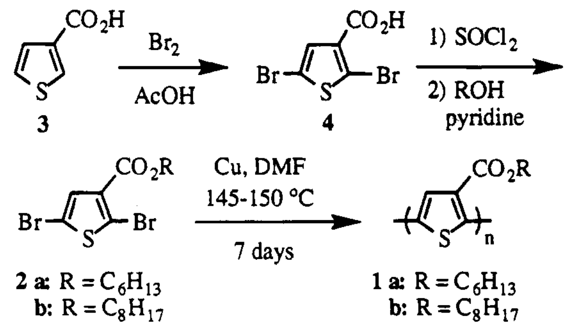
Scheme 1



H, $J = 7$ Hz), 1.73 (p, 2 H, $J = 7$ Hz), 1.2−1.5 (m, 10 H), 0.89 (t, 3 H, $J = 7$ Hz). ^{13}C NMR: δ 160.9, 132.0, 131.7, 119.0, 111.3, 65.5, 31.8, 29.2, 28.5, 26.0, 22.6, 14.1. IR: 3116, 2976, 2948, 2926, 2860, 2850, 1732, 1675, 1554, 1526, 1473, 1429, 1346, 1334, 1235, 1154, 1129, 1079, 1024, 1009, 974, 960, 900, 837, 766, 754, 720 cm^{-1}. UV−vis (THF): λ_{max} 240 nm (ϵ = 6800), 265 (ϵ = 5000), 275 (ϵ = 6200), 248 (sh), 251 (sh). Anal. Calcd for $C_{13}H_{18}O_2Br_2S$: C, 39.71; H, 4.09. Found: C, 39.71; H, 4.26.

Poly(alkyl thiophene-3-carboxylate) (1), General Procedure. Alkyl 2,5-dibromothiophene-3-carboxylate (**2**) (3.0 mmol), 0.58 g (9 mg-atom) of freshly prepared Cu powder,[11] weighed in a drybox, and 10 mL of dry DMF were put into a 25 mL flask equipped with a stirring bar and a long air condenser capped with a drying tube. The mixture was stirred at 145−150 °C for 7 days, cooled, and diluted with $CHCl_3$ to 200 mL, and then filtered to remove excess Cu powder. The red-orange organic phase was washed with water (10 × 100 mL) and dried ($MgSO_4$). Most of the $CHCl_3$ was removed with a rotary evaporator, the polymer was precipitated with MeOH, and the solid was extracted (Soxhlet) with methanol for 48 h. Drying under vacuum at room temperature gave the purple-red polymer **1**.

Poly(hexyl thiophene-3-carboxylate) (1a). Yield: 0.25 g (40%). ^{1}H NMR: δ 7.91 (br s), 7.85 (br s), 7.65 (br s), 7.59 (br s), 4.30 (br s), 4.14 (br s), 1.75 (br s), 1.54 (br s), 1.33 (br s), 1.24 (br s), 0.86 (br). ^{13}C NMR: δ 162.6, 162.5 (shoulder), 162.2, 162.1, 144−123 (approximately 15−18 peaks), 65.5, 65.3, 65.2, 31.4, 28.5, 28.4, 25.6, 22.5, 14.0. IR: 3085, 2958, 2929, 2856, 1720, 1710, 1464, 1401, 1343, 1261, 1197, 1122, 1019, 992, 847, 800, 774, 711 cm^{-1}. UV−vis: (THF) λ_{max} 423 nm, band edge 518 nm; film (cast from toluene), λ_{max} 447 nm, band edge 585 nm. GPC analysis gave a number average molecular weight ($\bar{M}_n$) of about 3030 with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 2.3. Anal. Calcd for $(C_{11}H_{14}O_2S)_n$: C, 62.83; H, 6.71; Br, 0.0. Found: C, 59.29; H, 5.58; Br, 0.0.

Poly(octyl thiophene-3-carboxylate) (1b). Yield: 0.40 g (56%). ^{1}H NMR: δ 7.92 (br s), 7.86 (br s), 7.66 (br s), 7.60 (br s), 4.30 (br s), 4.14 (br s), 1.75 (br s), 1.55 (br s), 1.23 (br), 0.87 (br s). ^{13}C NMR: δ 162.6, 162.4, 162.2, 162.1, 145−123 (approximately 15−18 peaks), 65.5, 65.4, 65.2, 31.8, 29.2, 28.54, 28.45, 26.0, 22.6, 14.0. IR: 3083, 2952, 2924, 2853, 1714, 1564, 1461, 1244, 1197, 1148, 989, 970, 848, 773, 722 cm^{-1}. UV−vis: (THF) λ_{max} 430 nm, band edge 530 nm; film (cast from toluene), λ_{max} 450 nm, band edge 565 nm. GPC analysis gave a number average molecular weight ($\bar{M}_n$) of about 4060 with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.9. Anal. Calcd for $(C_{13}H_{18}O_2S)_n$: C, 65.51; H, 7.61; Br, 0.0. Found: C, 62.40; H, 6.49; Br, 0.0.

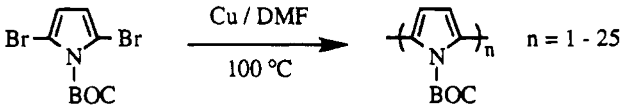
Results and Discussion

The synthesis of two polythiophenes containing the ester carbonyl directly attached to the thiophene ring, namely poly(hexyl thiophene-3-carboxylate) (**1a**) and poly(octyl thiophene-3-carboxylate) (**1b**) is shown in Scheme 1. 2,5-Dibromothiophene-3-carboxylic acid (**4**) was prepared essentially as described in the literature from **3**,[10] and this, in turn, was converted into hexyl and octyl 2,5-dibromothiophene-3-carboxylate (**2a** and **2b**). Treatment of **2a** or **2b** with freshly prepared copper powder[11] in DMF at 145−150 °C for 7 days, the Ullmann reaction, gave 40−56% yields of poly(hexyl thiophene-3-carboxylate) (**1a**) and poly(octyl thiophene-3-carboxylate (**1b**), respectively. Various properties of these polymers are given in Table 1.

Table 1. Properties of Polymers 1a and 1b Prepared by the Ullmann and Ni(0) Reactions

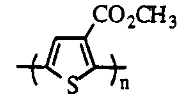
					fluorescence emission	
polymer (prep)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	λ_{max}^{THF} (nm)	λ_{max}^{film} (nm)	λ_{max}^{THF} (nm)	λ_{max}^{film} (nm)
1a (Cu)	3030	2.3	423	447	570	620
1b (Cu)	4060	1.9	430	450	568	630
1a [Ni(0)]	3050	3.2	408	429	555	595
1b [Ni(0)]	3510	2.8	408	430	555	600

There are many examples of the coupling of thiophenes[6−8] and the formation of oligothiophenes[4,5] using the Ullman reaction. In addition, there is a very recent report of the preparation of oligopyrroles, up to the 25-mer, by reaction of *N*-(*tert*-butoxycarbonyl)-2,5-dibromopyrrole with copper powder in DMF, shown in eq 1.[12]



(1)

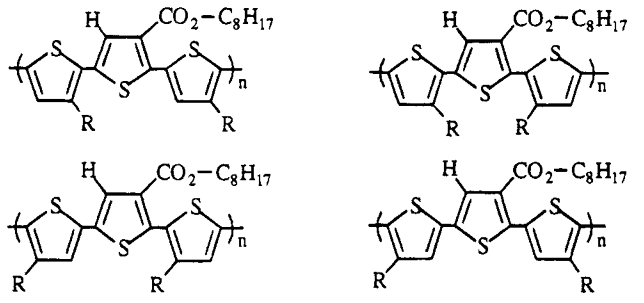
A related polymer containing positively charged nitrogen has also been reported recently,[13] and it should be mentioned, there are a number of reports of this reaction used to prepare oligo- and poly(*p*-phenylenes).[14] However, the present account is the first report of the use of the Ullmann reaction in forming polythiophenes. In 1992 Masuda and Kaeriyama reported on the preparation of poly(methyl thiophene-3-carboxylate) (**5**) using



5

methyl 2,5-dichlorothiophenecarboxylate and a Ni(0) catalyst, prepared from $NiBr_2$, Ph_3P, and Zn(0), in DMF (30 °C/60 h). The degree of polymerization reported was 13−18.[2] We have also used this Ni(0) coupling reaction with monomers **2a** and **2b** ($NiBr_2$, Ph_3P, Zn(0), DMF, 30 °C, 60 h) and obtained polymeric material. The properties of these materials are also presented in Table 1. As described below the material obtained from the Ullmann reaction was a better quality. Thus, while the polymers obtained from the Ullmann reaction were free flowing powders, those from the Ni(0) reaction were rather soft and sticky. Further, it should be noted that the Ni(0) conditions are not compatible with the variety of functional groups with which the Ullmann reaction is compatible. Thus the Ullmann reaction promises to be an exceedingly general method for the synthesis of a large variety of polythiophenes containing electron-withdrawing groups.

The polymers **1a** and **1b** were soluble in a variety of organic solvents such as $CHCl_3$, THF, DMF, CH_2Cl_2, benzene, toluene, and xylene. The spectral properties and the changes in the spectra upon going from **2** to **1** were consistent with the structure of the polymer. Thus, for example, the ^{13}C NMR spectral peaks for the C−Br carbons at δ 111.3 and 118.9 in **2a** and at 111.3 and 119.0 in **2b** were shifted to lower field in the polymers **1a** and **1b**. The IR spectra showed the C=O stretch at 1720 and 1714 cm^{-1}, and these IR spectra were similar to that of the methyl ester **5** reported by



$R = CO_2{-}C_8H_{17}$

Figure 1. The four H-H, H-T, and T-T triads.

Masuda and Kaeriyama ($\bar{\nu}_{C=O} = 1730\ cm^{-1}$).[2] The UV−vis absorption maxima of **1a** and **1b** in THF solution were 423 and 430 nm, respectively, and this was considerably longer than the 389 nm reported for **5**.[2] The absorption of the films cast from toluene were 447 and 450 nm, respectively.

For comparison, the polymers obtained from the Ni(0) reaction showed additional aromatic C−H absorptions in the ^1H NMR spectrum above the four absorptions which the polymers obtained from the Cu reaction showed. These four absorptions, which are not very different from one another in intensity, are due to the four head-to-head, head-to-tail, and tail-to-tail triads shown in Figure 1. This was confirmed by the observation of four closely spaced carbonyl peaks and three closely spaced *C*−O peaks, one with a shoulder, in the ^{13}C NMR spectrum. The ^{13}C spectra of **1a** and **1b** from the Ni(0) reaction also showed a number of additional peaks in the aromatic region over what was observed for the polymers prepared via the Ullmann reaction. Polymers **1a** and **1b** from the Ni(0) reaction showed their UV−vis absorption maxima at 408 nm for THF solutions and 429 and 430 nm for films cast from toluene. The wavelengths are blue shifted a fair amount from the absorptions of the polymers prepared by the Ullmann reaction and indicate that, as was observed with the methyl ester,[2] the conjugation length is considerably shorter.

Gel permeation chromatography (GPC) using polystyrene standards indicated number average molecular weights ($\overline{M}_n$) of around 3000−4000 (Table 1) with polydispersities ($\overline{M}_w/\overline{M}_n$) of 1.9−2.3 for **1a** and **1b** prepared with Cu while the polymers prepared with Ni(0) had $\overline{M}_n \approx 3000-3500$ with considerably larger polydispersities of 2.8−3.2. Thus the polymers prepared via the Ullmann reaction have about the same or slightly higher molecular weights than those prepared by the Ni(0) reaction, but more importantly there is a significantly narrower polydispersity in the former. This difference in polydispersity is probably a significant factor in making **1a** and **1b** from the Ni(0) reaction rather soft and sticky and from the Cu reaction free flowing powders. The average degree of polymerization ($\overline{DP}$), for these approximate molecular weights, is 14 and 17 for **1a** and **1b**, respectively, and is comparable to that reported for **5** (13−18).[2] An alternate way to obtain the molecular weight is by end group analysis if bromine remains on both ends of the polymer. Bromine analysis showed 0.0% Br for all four polymers, namely **1a** and **1b** from both the copper and Ni(0) reactions. Thus we could not obtain the molecular weight by this procedure.

Thermogravimetric analysis (TGA; N_2; 5 deg/min) of **1a** from the copper reaction showed the onset of decomposition at 310 °C, the maximum decomposition rate at about 400 °C, and 60% weight loss by 650 °C. **1b** (Cu reaction) showed essentially the same TGA curve, the onset of decomposition was at 320 °C, the maximum decomposition rate was at 400 °C and there was about 70% weight loss by 620 °C. The methyl ester **5** showed the onset of decomposition at 310 °C, and the maximum decomposition rate at 360 °C.[2] Thus **1a** and **1b** appear to be a little more thermally stable than **5**.

Films of polymers **1a** and **1b** showed bright red-orange and red fluorescence, respectively, under UV light, and thus their fluorescence properties were examined. Using exciting light of 465−500 nm (where it was determined the fluorescence showed maximum intensity), THF solutions of the two polymers from the copper reaction showed emission maxima at 570 and 568 nm, respectively, while films cast from toluene showed emission maxima for **1a** and **1b** at 620 and 630 nm, respectively. The Ni(0) polymers **1a** and **1b** showed THF solution emission at 555 nm and toluene-cast film emission 595 and 600 nm, respectively. Once again this confirms the longer conjugation lengths in the polymers prepared by the Ullmann reaction (Table 1).

In summary, we have shown that soluble polythiophenes with electron-withdrawing ester groups attached at the 3-position can be synthesized by the Ullmann reaction using copper powder in DMF. Poly(hexyl thiophene-3-carboxylate) (**1a**) and poly(octyl thiophene-3-carboxylate) (**1b**) have been prepared and characterized. The polymers prepared by this route have better properties than those prepared by the Ni(0) coupling reaction.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of poly(hexyl thiophene-3-carboxylate) (**1a**) and poly(octyl thiophene-3-carboxylate) (**1b**) prepared by both the Ullmann and Ni(0) reactions (8 pages). Ordering information is given on any current masthead page.

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