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Thallium(III) Trifluoroacetate−Trifluoroacetic Acid in the Chemistry of Polythiophenes. 1. Polymers from 2,2′-Bithiophene and 2,2′,5′,2″-Terthiophene. Mechanistic Aspects

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A new chemical method of simultaneous polymerization and doping of 2,2′-bithiophene (**1**) and 2,2′,5′,2″-terthiophene (**2**) using thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA) is reported. These reactions have been carried out at 20 °C and at 72 °C observing no remarkable differences in the quality of the polymers, which are undoped or compensated and purified to their neutral state by extraction with different solvents, and redoped in I_2 atmosphere. Infrared spectra and conductivity measurements of the polymers, either as grown from the reaction mixture or after being redoped with I_2, qualify them as good semiconductors, and their electron paramagnetic resonance (EPR) spectra show characteristic single lines with Lorentzian shapes and narrow line widths attributed to unpaired electrons delocalized along the carbon backbone chains. 2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2‴″-Sexithiophene (α-sexithiophene; **3**) has been isolated and identified from one of the polymers during the purification process. EPR of the radical cation of **3** in CH_2Cl_2−TFA shows a symmetric multiplet which consists of a quintet (a_{4H} = 2.18 G) of septets (a_{6H} = 1.10 G). Variable-temperature EPR studies of **3** revealed the formation of its diamagnetic π-dimer at low temperature in equilibrium with the radical cation. EPR and electronic spectra of reaction mixtures of **1** and **2** with TTFA/TFA show that **3** is the shortest oligomer whose radical cation is stable enough to be detected. **2** is protonated in TFA and it is suggested that **2** dimerizes to **3** in the presence of TTFA, through an oxidative coupling involving its conjugate acid.

Introduction

It has been demonstrated that solutions of thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA) constitute a powerful reagent for the direct thallation of aromatic compounds.[2] The products obtained are versatile intermediates for aromatic substitution reactions. Thus, one of the most extensive iodination methods of substituted benzenes utilizes the formation of arylthallium bis(trifluoroacetate) intermediates with TTFA/TFA mixtures to subsequently treat them with an aqueous potassium iodide mixture. In this way, many iodobenzenes were prepared in excellent yields.[3]

But thallation represents a particularly relevant example of electrophilic aromatic substitution, because Kochi *et al.* showed the presence of radical cations of the corresponding arenes by electron paramagnetic resonance (EPR) upon treatment under thallation conditions.[4] Thus, thallium(III) can act as a one-electron oxidant of many aromatic substrates.[5] In fact, reduction of Tl(III) to Tl(I) is an especially favorable process ($E°$ = −1.25 V).

In several cases, reactions of arenes with TTFA/TFA led to oxidative dehydrodimerization of the organic compound instead of electrophilic thallation, depending on the substrate, suggesting that the intermediate radical cation formed in the process reacts with a molecule of the substrate to finally give the biaryl through a subsequent oxidation.[6]

In the course of the investigations[7] to obtain radical cations from different aromatic substrates, some of us were able to detect for the first time the radical cations of some heteroaromatic compounds, when solutions of these substrates in TFA were photolyzed in the same cavity of the EPR spectrometer in the presence of TTFA. Thus, furans, thiophenes, pyrroles, and more recently, 2,2′-bithiophenes (α-bithiophenes; **1**) in TTFA/TFA generated radical cations, which were stable enough to be detected and studied by EPR spectroscopy when they were substituted by alkyl groups.[7]

When thiophene and pyrrole were each treated with TTFA/TFA, they gave rise to very dark solutions and a black solid separated in a few minutes. Some preliminary results reported in the case of thiophene, confirmed that this solid, most probably a polymeric material which contained oxygen, was very stable, showed a strong singlet in the EPR spectrum (g = 2.0034; ΔH_{pp} = 1.45

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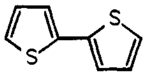
G), and exhibited a moderate electrical conductivity ($\sigma \simeq 2 \times 10^{-3}\ \Omega^{-1} \times \mathrm{cm}^{-1}$).[8]

Although the most extensive method to prepare electroconductive polymers is the electrochemical polymerization, there are some chemical methods which produce polymers of good quality and electrical properties.[9] One is the Grignard coupling reaction from 2,5-dihalothiophenes, where the polymer is obtained in its insulating form and can be further doped to a conductor state.[10] The one-step chemical synthesis of doped polythiophenes, which consisted of simultaneous oxidative polymerization and doping, constitute another interesting approach to these materials,[11] particularly those concerning $FeCl_3$ both as initiator and dopant which produce doped polythiophenes of high quality.[11d-g]

McKillop *et al.* reported that TTFA was an efficient reagent for thiophene and some 2-substituted derivatives in electrophilic thallations if acetonitrile was used as solvent instead of TFA.[3a,c]

Encouraged by this and as part of our efforts to get electroconductive polythiophenes by means of chemical methods, we now report on the polymerization of two oligomers, α-bithiophene (**1**) and 2,2′,5′,2″-terthiophene (α-terthiophene; **2**), when they are subjected to the action of TTFA/TFA. Our results indicate the oxidant properties of this mixture to obtain doped polymers. In the course of our investigations, we have detected as well as studied by EPR and electronic spectra the radical cation of 2,2′,5′,2″,5″,2‴,5‴,2⁗,5⁗,2′′′′′-sexithiophene (α-sexithiophene; **3**).



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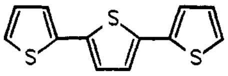

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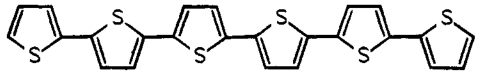

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Results and Discussion

Preparation of Polymers. Polythiophenes were prepared from **1** or **2** with TTFA (1:1 molar proportion) in TFA. The solution turned blue immediately after adding the thallium salt and had a deeper color with time while a precipitate appeared in the medium. The products and reaction conditions are summarized in Table 1 together with the analytical data. The composition of the products show the presence of fluorine and oxygen, and the carbon and sulfur content is smaller than for a neutral polymer $(C_4H_2S)_n$. These results suggest that a light doping occurs simultaneously with the polymer synthesis.

Table 1. Reaction Temperature and Chemical Composition of As Grown Polymers

			anal. % found				
polymer	monomer	temp (°C)	C	H	S	F	O
4	**1**	20	56.4	2.3	35.7	1.0	2.9
5	**1**	reflux	55.7	2.0	37.1	1.6	2.2
6	**2**	20	56.5	2.3	38.0	0.7	2.2
7	**2**	reflux	56.2	2.3	37.6	0.8	2.0

Table 2. Yields and Chemical Composition of Neutral Polymers

		anal. % found[c]			
polymer[a]	yield, %[b]	C	H	S	total
4	95	58.0	2.5	38.2	98.7
5	96	57.8	2.5	38.2	98.5
6	99	58.5	2.6	38.9	100
7	98	58.0	2.5	38.9	99.4

[a] The polymers are enumerated as in Table 1. [b] Calculated for neutral $(C_4H_2S)_n$. [c] Calculated for neutral $(C_4H_2S)_n$: C, 58.5; H, 2.5; S, 39.0.

Table 3. Chemical Composition of Iodine-Doped Polymers

	anal. % found					
polymer[a]	C	H	S	I	total	empirical formula
4	50.9	2.1	34.2	11.4	98.6	$C_{3.97}H_{1.95}S_{1.0}I_{0.08}$
5	52.5	2.0	35.3	9.3	99.1	$C_{3.97}H_{1.8}S_{1.0}I_{0.07}$
6	51.9	2.2	34.7	10.9	99.7	$C_{4.00}H_{2.02}S_{1.0}I_{0.08}$
7	52.4	2.2	35.4	9.5	99.5	$C_{3.94}H_{1.98}S_{1.0}I_{0.07}$

[a] The polymers are enumerated as in Table 1.

Fluorine and part of the oxygen content may be accounted for by trifluoroacetate ion in the product to neutralize the defect charges (polarons and/or bipolarons) induced by oxidation of the polymer. Further, part of the oxygen might be attributed to a possible intercalation of hydroxide ion, since a charge-transfer complex between O_2 and the chains is not probable due to the stability of neutral polymer in air.

The doped products were purified by the use of a Soxhlet extractor with various solvents. First, ethanol to remove polar impurities, and then chloroform, tetrahydrofuran and chlorobenzene to remove low and medium-molecular weight fractions were used, respectively. Analytical data of the products are displayed in Table 2.

During the treatment with ethanol, the insoluble products changed from dark brown to reddish brown, and the composition of the final materials showed a close agreement with that calculated for the neutral polymer $(C_4H_2S)_n$. Thus, washing with hot ethanol results in a practically complete undoping. In all cases, particularly in polymer **7**, the chlorobenzene extractions left a yellow solid, identified as α-sexithiophene (**3**) by infrared and mass spectra.

The compensated or undoped products were exposed to iodine vapors to be redoped. Analytical data of the resulting dark brown polymers are given in Table 3. The empirical formulas show a small content of iodine, suggesting an oxidation of the powdery solids when exposed to iodine. A thermogravimetric (TG) analysis of iodinated polymers **5** and **7** showed a loss of weight (10 and 13% for **5** and **7**, respectively) at about 130 °C,

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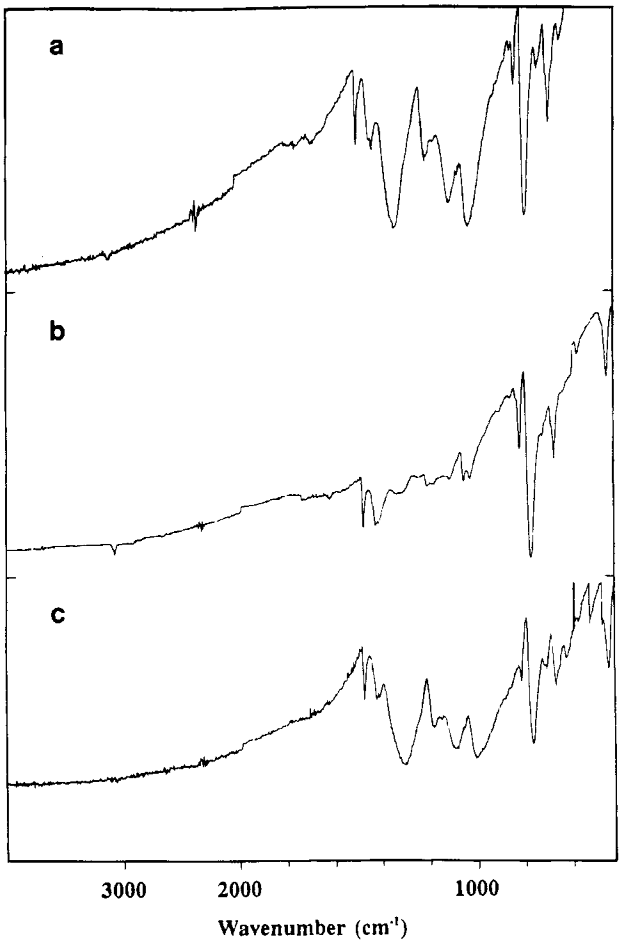

Figure 1. Infrared spectra in KBr of (a) as grown polymer **7**, (b) the neutral polymer **7**, and (c) the iodine-doped polymer **7**.

which corresponded to the loss of iodine and their conversion to neutral polymers (IR).[12]

Infrared (IR) Spectroscopy. As an example, typical IR spectra of polymer **7**, as grown and after iodine doping, are displayed in Figure 1, parts a and c, respectively. Each spectrum showed well-defined and broad bands at approximately 1320, 1200, 1110, and 1010 cm^{-1} that are characteristic of doped polythiophenes; the bands corresponding to the as grown polymer being sharper. Thus, IR data provide evidence that polymerization and doping occurs simultaneously.

Figure 1b shows the IR spectrum of the compensated and purified polymer **7**. The strong and sharp band at about 790 cm^{-1} corresponds to the out-of-plane C–H vibration band characteristic of 2,5-disubstituted thiophenes.[10a] The small band at 730 and the band at 830 cm^{-1} may be attributed to the small fraction of 2,4-thienylene units incorporated into the polymer,[10a] although the latter also appears in the spectrum of polythiophene obtained through a Grignard condensation of 2,5-dihalothiophenes, which should have a well-defined 2,5-substitution pattern due to the synthetic route.[10b]

Table 4. EPR Spectral Data and Conductivity of Polymers 4–7

polymer[a]		g	ΔH_{pp}(G)	σ^c(Ω^{-1} cm^{-1})
4	as grown	2.0028	3.02	3.3×10^{-2}
	after doped with I_2	2.0036	3.6	6.0×10^{-3}
5	as grown	2.0027	1.62	1.0×10^{-3}
	after doped with I_2	2.0033	3.2	1.4×10^{-3}
6	as grown	2.0027	1.70	0.85×10^{-4}
	after doped with I_2	2.0030	3.9	2.7×10^{-1}
7	as grown	2.0027	1.70	1.6×10^{-2}
	after doped with I_2	2.0032	4.0	2.5×10^{-2}

[a] Polymers are enumerated as in Table 1. [b] ΔH_{pp}: peak to peak line width of the first derivative of the absorption curve. [c] σ: conductivity at 20 °C on pressed pellets.

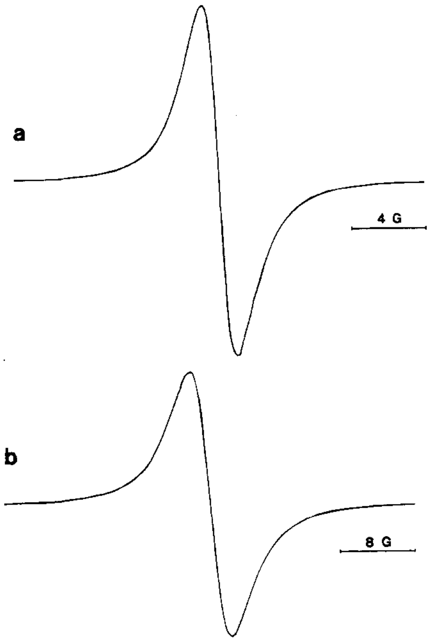

Figure 2. EPR spectra of (a) as grown and (b) I_2-doped polythiophene **7** at 20 °C.

Electron Paramagnetic Resonance (EPR). The description of the magnetic properties of polythiophenes in their doped or undoped states, which are related to the paramagnetic centers delocalized along the polymer chains, have been extensively studied by EPR spectroscopy.[13] All polymers **4–7**, either as grown from the polymerization medium or after doping with I_2, display single lines with Lorentzian shapes, as shown by simulation of the spectra, corresponding to unpaired electrons delocalized along the carbon backbones. The g-factors and line widths are shown in Table 4. As an example, Figure 2 shows the EPR spectra of the as grown and I_2-doped polythiophene **7**.

Conductivity Measurements. The electrical conductivity of polymers **4–7**, as grown and after doping with I_2, were measured on compressed pellets at 20 °C by the four-probe method.[14] The values given in Table 4 show the same order of conductivities as those reported[13] for other chemically synthesized polythiophenes.

Some Mechanistic Aspects. EPR spectroscopy provides an excellent method of detecting and studying radical cations of homo- and heteroarenes oxidized by chemical or electrochemical procedures.

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(12) Some reported studies on the variation of optical spectroscopy and conductivities of doped polythiophenes have concluded that undoping processes take place with temperature: Hotta, S.; Soga, M.; Sonode, N. *Synth. Met.* **1988**, *26*, 267. Gustafsson, G.; Inganäs, O.; Nilsson, J. O. *Synth. Met.* **1989**, *28*, C 427. Wang, Y.; Rubner, M. F. *Synth. Met.* **1990**, *39*, 153.

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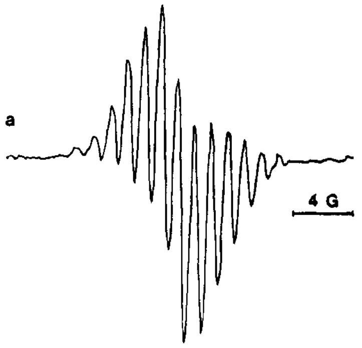

Figure 3. (a) EPR spectrum of a solution of **1** in TFA with TTFA, (b) after 1 h, (c) after removal of the precipitate.

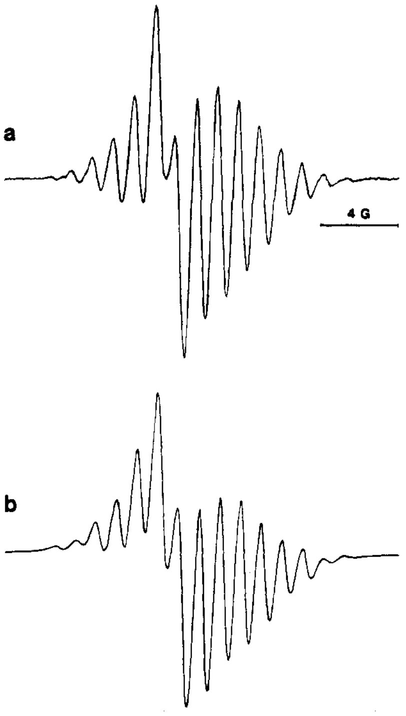

Figure 4. (a) EPR spectrum of a solution of **2** in TFA with TTFA. (b) Computer simulation as a combination of two spectra: (1) radical cation of **3** and (2) a single line of Lorentzian shape (g = 2.0031; ΔH_{pp} = 1.56 G).

As noted above, the EPR spectra of radical cations of simple heteroarenes as furans, pyrroles, and thiophenes have been detected in fluid solution when they were substituted in the 2- and 5-positions by alkyl groups.[7a–e] In this way, we have been able to generate radical cations of some α-bithiophenes, with their terminal α-carbons blocked with alkyl groups, and to study by EPR the hyperfine coupling (hfc) constants between the unpaired electron and the protons in the molecule.[7f] Although generation of the unsubstituted α-bithiophene radical cation by oxidation of **1** in CH_2Cl_2/TFA (1:1) was claimed,[15] its assignment was not unambiguous.

To study the mechanism of polymerization of **1** and **2** by means of TTFA/TFA, we examined these mixtures by EPR in diluted conditions. When a solution of TTFA in TFA (10^{-3} M) was poured into a solution of **1** in TFA (10^{-3} M) in a 0.8:1 molar proportion, an intense blue color developed. If this solution was checked by EPR, the spectrum of Figure 3a was obtained, which evolved into the spectrum of Figure 3b after approximately 1 h while a small precipitate appeared. If this mixture was filtered, the solution displayed the spectrum of Figure 3c. The spectra in Figure 3, parts a and b, appear to be an overlap of two types of lines: a broad singlet which increases with the precipitate, and a symmetric multiplet which remains constant, and corresponds to a species in solution (Figure 3c). Solutions of **2** (10^{-3} M) in TFA with TTFA (1:2 molar proportion) gave the spectrum in Figure 4a. This spectrum consists of a multiplet, identical to that of **1**, and a singlet which now corresponds to a species in solution. The symmetric multiplet, common to both oligomers, coincides with the spectrum when saturated solutions of **3** in TFA are analyzed by EPR. Thus, although **3** is very insoluble in TFA at 20 °C, it develops green solutions when heated. The EPR multiplet of them is attributed to the **3** radical cation (**6T**$^{\cdot+}$). Thus, while **1** and **2** are stable in TFA, higher oligomers, **3**, undergo rapid oxidation to the radical cation as a consequence of the decreasing values of redox potentials with increasing number of thienyl rings.[16] A more satisfactory EPR spectrum of **6T**$^{\cdot+}$ can be obtained when a CH_2Cl_2 solution of **3** with a small amount of TFA is put into the cavity of the spectrometer; a strong, symmetric, well-resolved spectrum of Figure 5a is displayed. The computer-simulated spectrum (Figure 5b), assuming it arises from a single radical species, is consistent with the experimental spectrum and shows the following parameters: g = 2.0021 and peak to peak line width, ΔH_{pp} = 0.45 G. The hyperfine splitting corresponds to coupling of the electron spin with four hydrogens a_{4H} = 2.18 G, and six hydrogens a_{6H} = 1.10 G. Hyperfine coupling to the four other hydrogens in the molecule have been ignored in the simulation, since they should be too small to be detected. Theoretical estimation of the hfc constants for the radical cation of α-sexithiophene has been carried out using McLachlan's method. The heteroatom parameters h_M corresponding to the Coulomb integral, $\alpha_M = \alpha + h_M\beta$ and k_{CM} of the resonance integral $\beta_{CM} = k_{CM}\beta$ are 1.0 and

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(16) **1** and **2** are initially stable in TFA, but they decompose after a few hours probably due to oxygen in solution.

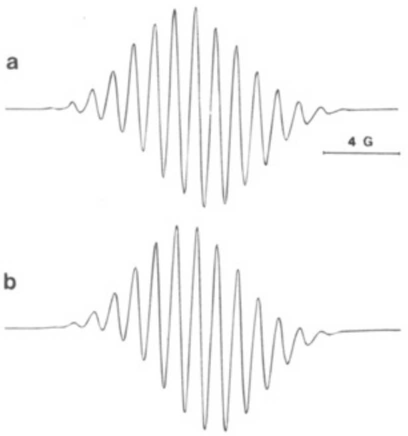
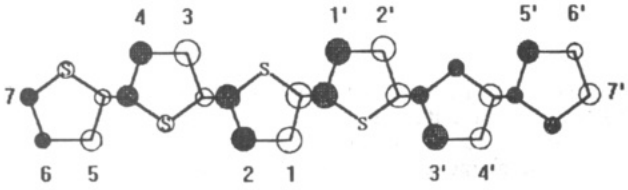


Figure 5. (a) EPR spectra of the cation radical of saturated solutions of **3** in TFA at 20 °C. (b) Computer simulation using the splitting constants given in the text.

0.86 for S, respectively.[17] Thus, the SOMO of the radical cation **6T**$^{\cdot+}$ has the following form:



The values of calculated hfs constant are $a_{1,1'} = 1.80$; $a_{2,2'} = 1.19$; $a_{3,3'} = 1.66$; $a_{4,4'} = 0.34$; $a_{5,5'} = 1.00$; $a_{6,6'} = -0.13$; $a_{7,7'} = 1.07$. These values are in good agreement with those used in the spectral simulation of **6T**$^{\cdot+}$. The signal intensity decreases very rapidly and in a few minutes a new and less intense broad singlet slowly appears. This singlet is presumably due to radical species from higher oligomers which appear in the medium as the result of polymerization of **3**. Singlets in the spectra of solutions of **1** and **2** mentioned above can be accounted for by similar reasons.

Thus, in Figure 4b a simulation of the spectrum in Figure 4a, which corresponds to the oxidation of **2**, is displayed. This simulation corresponds to a combination of two signals: one multiplet attributed to the **6T**$^{\cdot+}$ and one singlet (Lorentzian shape, $g = 2.0031$, $\Delta H_{pp} = 1.56$ G) attributed to the radical cations of higher oligomers.

In order to stabilize the cation radical **6T**$^{\cdot+}$, more dilute solutions of **3** in CH_2Cl_2 with some TFA were examined by EPR, and the signal intensities have been studied at variable temperature. On cooling, the signal slowly decreased so that at about −40 °C the signal was about 50% as intense as at 20 °C, and at −70 °C the signal practically dissappeared; the process was reversible. As reported[19] for shorter oligomers, at low temperatures the radical cations of **3** associate through weak bonds to form doubly charged singlet dimers, which are not EPR active.

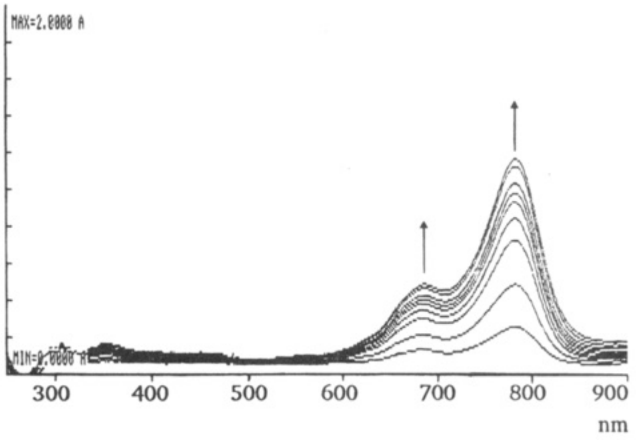
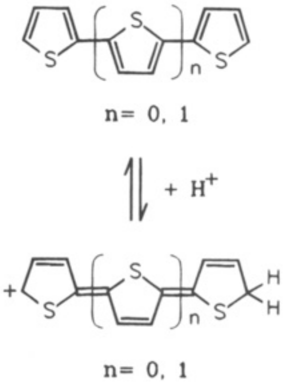


Figure 6. UV-vis spectra of solutions of **3** in CH_2Cl_2 with some drops of TFA. Spectra recorded every 3 min (λ_{max} 677 and 765 nm).

Scheme 1



The electronic spectra of **1** and **2** in $CHCl_3$ display one band at λ, 302 and 355 nm, respectively,[20] while in TFA the electronic spectra of both oligomers display two bands: for **1** at λ, 307 and 411 nm, and for **2** at λ, 322 and 531 nm. In mixtures of $CHCl_3$ and TFA, both oligomers show similar bands as in TFA with relative intensities depending on the proportion of TFA. These observations indicate the existence in acidic media of equilibria between neutral oligomers and their conjugate acids (Scheme 1), being the bands at longer wavelengths presumably due to the charged species. For **2**, this equilibrium must be shifted to the right side because of the low intensity of the transition at λ, 322 nm.

Electronic spectra of very dilute CH_2Cl_2 solutions of **3** with a few drops of TFA (Figure 6) consist of two bands at λ, 677 and 765 nm, ascribed to **6T**$^{\cdot+}$ (literature values[21] of λ, 682 and 780 nm in CH_2Cl_2) consistent with the EPR spectrum. Absorption intensities of these bands initially increased and then decreased while new transitions emerge at longer wavelengths.

Electronic spectra of **2** in TFA (10^{-4}–10^{-5} M) in the presence of TTFA are displayed in Figure 7. During the oxidation, the band at λ 532 nm, attributed to its conjugate acid, decreased while those corresponding to the **6T**$^{\cdot+}$ increased, also consistent with the detection of the signal of **6T**$^{\cdot+}$ in EPR analysis.

Thus, in the polymerization process, **2** dimerizes to **3** in TFA with TTFA through an oxidative coupling mechanism involving its conjugate acid (Scheme 2).[22]

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(17) These parameters have been used in our calculations to provide good hfs constants for the substituted derivatives of α-bithiophene radical ions,[7f] and they are modified from those published in the literature.[18]

(18) Allred, A. L.; Bush, L. W. *J. Am. Chem. Soc.* **1968**, *90*, 3352. Bock, H.; Roth, B. *Phosphorus Sulfur* **1983**, *14*, 211.

(19) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728. Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

(20) Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B.; Van Pham, Ch.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021.

(21) Fichou, D.; Horowitz, G.; Garnier, F. *Synth. Met.* **1990**, *39*, 125.

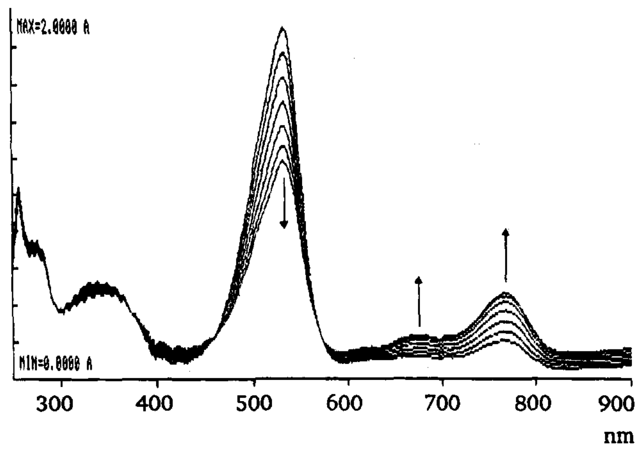


Figure 7. UV-vis spectra of solutions of **2** in TFA (6 × 10^{-5}M) with TTFA. Spectra recorded every 10 min (λ_{max} 533, 676, and 768 nm).

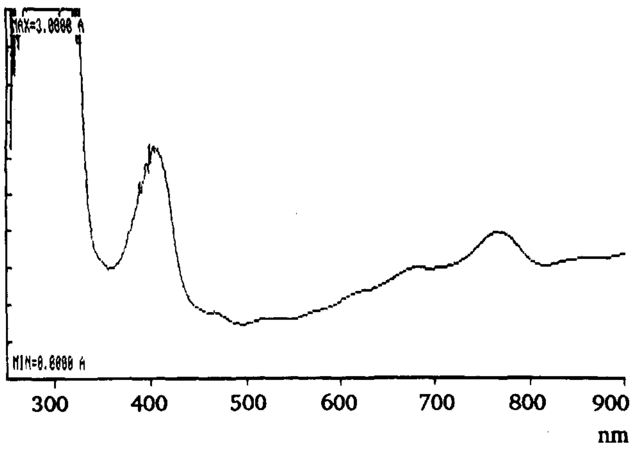
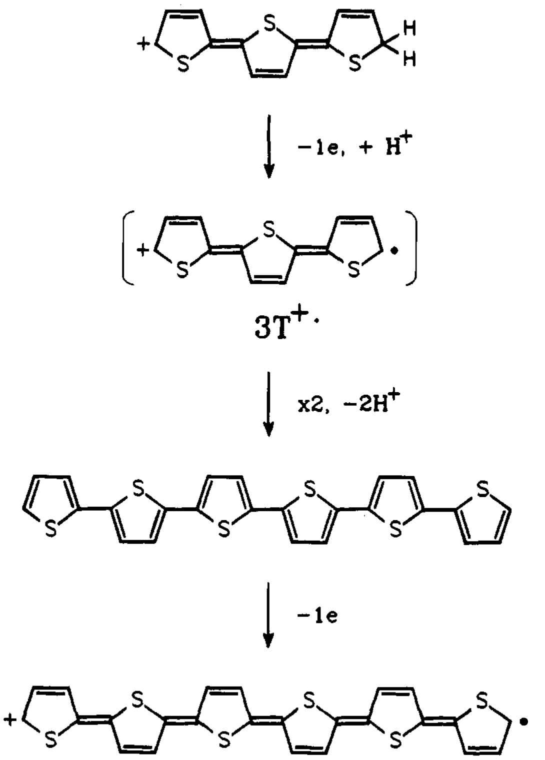


Figure 8. UV-vis spectra of solutions of **1** in TFA containing TTFA.

Scheme 2



Although much more complex, spectra of **1** in TFA containing TTFA also display bands at λ 685 and 770 nm, attributed to the **6T**$^{\cdot+}$ (Figure 8). In this case, neutral and cationic species of **1** are in equilibrium in the acidic medium and the oxidative action of TTFA may involve both species. All the observations from EPR and electronic analyses of the oxidative polymerization of **1** or **2** are consistent with the fact that **3** is the shortest oligomer whose radical cation is stable enough to be detected.

Conclusions

We have found a one-step chemical polymerization and doping of α-bithiophene and α-terthiophene using TTFA in TFA as oxidant. This polymerization produces powdery solids whose conductivities are into the same order as those in the literature, and it has the advantage over the electrochemical routes due to easy mass production in shorter reaction times. We have shown by EPR and electronic spectra that the radical cation of **3** is a common intermediate either in the polymerization of **1** or in that of **2**. We have also shown by EPR that dilute solutions of **3** in TFA display its radical cation initially as a multiplet, as the result of the coupling of the free electron with two groups of hydrogens in the molecule. Hyperfine coupling constants have been assigned by theoretical estimations using McLachlan's method. Studies at low temperatures have confirmed that **3** radical cation most probably forms a diamagnetic dimer in a reversible way. The influence of solubilities of polymers with long alkyl chains is in progress.

Experimental Section

General Procedures. **1** was used as received and **2** was prepared as reported.[23] TTFA was used as received and TFA was distilled before use. The synthesis of polymers were performed under argon. The IR spectra were recorded on KBr pellets by the use of a Perkin-Elmer Model 682 spectrometer. The UV-vis spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrometer coupled with a Perkin-Elmer 7300 computer. The thermogravimetric curves were obtained with a Perkin-Elmer TGS-1 thermobalance under N_2. The electrical conductivities were determined on compressed pellets by van der Pauw's four-probe method.

EPR Experiments. EPR spectra were recorded using a Varian E 109 spectrometer working in the X band and using a Varian E-257 temperature-controller. The EPR simulations were carried out with a Hewlett-Packard 9835-B computer using a modified version of a Varian E-935 Data Acquisition System. To detect radical species, solutions of **1** and **2** (10^{-3}–10^{-5} M) in TFA containing TTFA, saturated solutions of **3** in TFA, and solutions of **3** (10^{-4} M) in CH_2Cl_2 containing drops of TFA were degassed by passing a stream of dry argon through the solution to remove oxygen and then inserted into the cavity of the spectrometer.

Preparation of Doped Polymers. General Procedure. A (1:1 molar proportion) solution of TTFA in TFA (15 mL) was added dropwise at 20 °C to a stirred solution of **1** or **2** (1.00 g) in TFA (10 mL). The mixture was then stirred at 20 °C or at reflux for additional time (24 h) and filtered. The precipitate was washed with an excess of TFA and then a large amount of water and dried in vacuum (0.9 mmHg; 60 °C; 2 h).

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(22) Detection of the radical cation from hexamethylcyclopentadiene in TFA was interpreted to involve photolysis of its conjugate acid: Courtneidge, J. L.; Davies, A. G.; Gregory, P. S.; Yazdi, S. N. *Faraday Discuss. Chem. Soc.* **1984**, *74*, 1. Courtneidge, J. L.; Davies, A. G. *Bull. Soc. Chim. Belg.* **1984**, *93*, 329.

(23) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347.

Temperature conditions and analytical data of the dark brown precipitates are given in Table 1.

Compensation of the Polymers. The polymers were purified by the use of a Soxhlet extractor with different solvents. Initially with ethanol (8 h) at reflux, and then with $CHCl_3$ (2 h), THF (2 h), and chlorobenzene (2 h) at reflux. All the organic solutions gave, upon evaporation, small quantities of residues. Only in the polymer from **2** in TFA at reflux, the chlorobenzene fraction gave a very small yield of **3** (≃5%) identified by IR[24] and UV[25] spectra. MS *m*/*e* 494 (100%, M^+), 247 (18%, M^{2+}). Analytical data of the reddish brown residues are displayed in Table 2.

Doping of Neutral Polymers with I_2. The neutral polymers were exposed to I_2 vapors at atmospheric pressure (4 days) and dried in vacuum (0.05 mmHg; 60 °C; 1 h). Analytical data are given in Table 3.

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[24] Furukawa, Y.; Akimoto, M.; Harada, I. *Synth. Met.* **1987**, *18*, 157.

[25] Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B.; Van Pham, Ch.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021.