

A Novel Approach to a One-Pot Synthesis of Unsubstituted Oligo(α -thiophenes)

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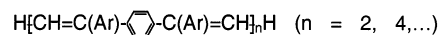
Abstract: Oligo(α -thiophenes) α -4T and α -8T were prepared by the following one-pot sequential conversions: thiophene (T) \rightarrow α -2T \rightarrow α -4T \rightarrow α -8T. PdCl₂-induced coupling of a mono- α -mercuration derivative of each of the n -mers T, α -2T, and α -4T was applied in these conversions.

Oligo(α -thiophenes) exhibit many of the desirable electrooptical characteristics of the derived polymers.¹ Their extensive α -electron conjugation led to a large number of optoelectronic applications such as active layers in field effect transistors,² light emitting diodes,³ photovoltaic cells,⁴ etc. Despite the resulting wide interest in unsubstituted oligo(α -thiophenes), the reported synthetic routes to these oligomers (α -4T, α -5T, α -6T, α -8T) are limited. A two-step-synthesis approach was used in all the reported syntheses of these oligomers. First, an α -monofunctionalized thiophene n -mer ($n = 1-4$) was prepared and then coupled to yield the target oligomers. Coupling of α -lithiated thiophene n -mers in the presence of CuCl₂,⁵ FeCl₃,⁶ and ferric acetylacetonate⁶ has often been used. Oligo(α -thiophenes) were also prepared by reacting the α -magnesium halide derivatives with α -bromothiophene in the presence of NiCl₂(dppp).⁷ All existing approaches involve isolation and purification of each n -mer prior to its conversion to the corresponding ($n + 1$)-mer or $2n$ -mer. The recently reported solid-phase synthesis of oligo(α -T)⁸ represents a significant improvement in this regard.

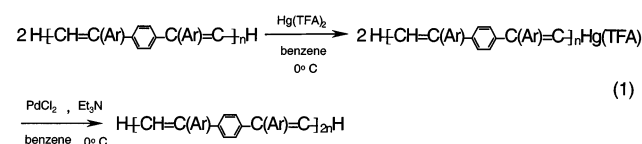
A general, relatively efficient one-pot approach to long-chain conjugated oligomers was recently introduced in an excellent review on linear monodispersed conjugated oligomers.⁹ It consists of homo- or hetero-coupling reactions of symmetrical conjugated oligomers, heterocycles,

etc. These, however, are statistical oligomerization systems which lack the critically required control over oligoselectivity and therefore yield low amounts of the particular oligomers.

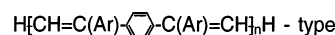
We recently reported a conceptually novel approach to an efficient one-pot stepwise synthesis of monodispersed oligomeric PPV-analogues, having extended π -conjugation.¹⁰ Oligomers of the general structure



were prepared from the corresponding conjugated difunctional symmetrical monomer ($n = 1$). This approach was based on repeatedly performing a sequence of two reactions: a selective monofunctionalization of the conjugated dienic n -mer (starting with $n = 1$), followed by coupling of the product of this reaction to yield the corresponding $2n$ -mer (eq 1). Reactions similar to those



involved in the one-pot synthesis of the



oligomers¹⁰ were applied in a two-step dimerization of thiophene to yield α, α' -bithienyl (Scheme 1):

It was, therefore, the purpose of the present research to adjust and apply the approach used for preparing the above-mentioned oligomeric PPV analogues¹⁰ for an analogous novel one-pot synthesis of oligo(α -thiophenes). A specific objective in this regard was the one-pot stepwise conversion of thiophene to α -8T by the following series of consecutive dimerization reactions: T \rightarrow α -2T \rightarrow α -4T \rightarrow α -8T.

We succeeded (in the first phase of this research) in converting the above two-step synthesis of α, α' -bithienyl (Scheme 1) into an efficient general one-pot dimerization, applicable for converting oligo(α -thiophene) n -mers to the corresponding $2n$ -mers. The dimerization of each thiophene α -2T and α -4T was performed by consecutively carrying out, in one pot, the following two reactions: (a) reaction of the substrate (α - n T, $n = 1, 2, 4$) with Hg(TFA)₂ to yield the corresponding mono- α -HgTFA derivative, and (b) PdCl₂-induced coupling of this mercuration product (Scheme 1). The reactions were carried out in benzene at low temperatures (0–5 °C) and in relatively short reaction times.

The experimental conditions involved and the results obtained are summarized in Table 1. The corresponding dimerization products, α -2T from T (entries 1, 2), α -4T from α -2T (entry 5), and α -8T from α -4T (entry 7), respectively, were obtained in high yields.

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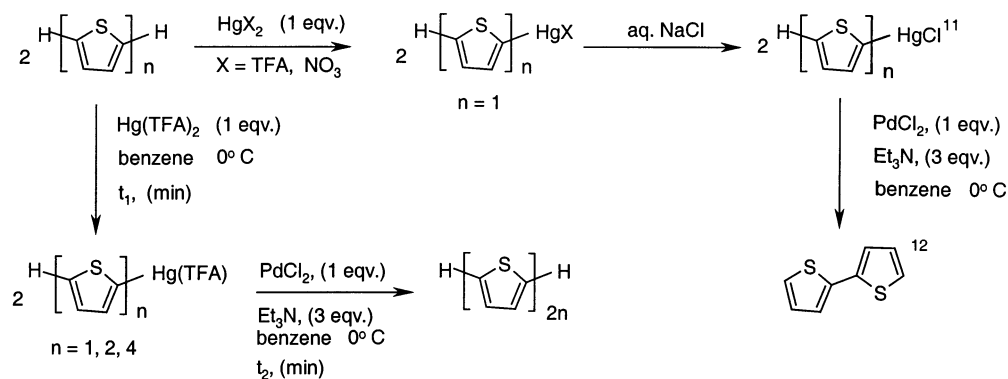
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SCHEME 1

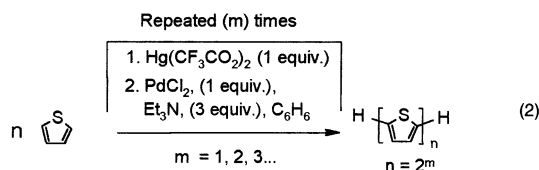
TABLE 1. One-Pot Stepwise Preparation of Oligo(α -thiophenes) Experimental Conditions^a and Results

entry	starting thiophene	reaction time, min		product(s)	yield ^b (%)
		t_1	t_2		
1	T	15	15	α -2T	89
2	T	5	10	α -2T	92
3	T	15	15	α -4T + (α -2T)	76 + (5)
4	T	15	15	α -8T + (α -4T) + (α -6T)	70 + (18) + (2-3)
		15	15		
		15	15		
5	α -2T	15	15	α -4T	88
6	α -2T	15	15	α -8T + (α -4T) + (α -6T)	81 + (7) + (2-3)
		15	15		
7	α -4T	15	15	α -8T	80

^a The temperature of the reaction mixture throughout the reaction was 0–5 °C. ^b Isolated yields of the target n -mer.

The high efficiency of these dimerization reactions of α - n T ($n = 1, 2, 4$) clearly points to an exclusive mercuration (in the presence of 1 equiv of Hg(TFA)₂) at one of the two α -positions of the oligo(α -thiophene). This suggests that the presence of the HgTFA substituent effectively suppresses the mercuration at the other unsubstituted α -position.

The relatively high efficiency observed in each of the three one-pot dimerization reactions (to yield α -2T, α -4T, and α -8T) led to the application of this experiment protocol for conducting the following one-pot conversions, without isolating any of the intermediate products: (a) thiophene to α -4T, (b) thiophene to α -8T, and (c) α -2T to α -8T. The results are summarized in Table 1. This novel approach to oligo(α -thiophenes) and the derived methodology may be presented as follows (eq 2):

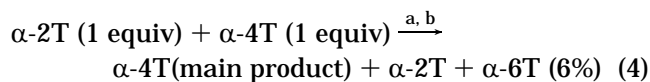
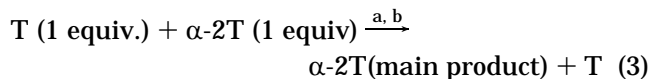


Thus, for example, the one-pot 8T \rightarrow α -8T conversion (entry 4) involved steps 1 and 2 (eq 2) to yield (in situ) α -2T, the reaction time being t_1 and t_2 , respectively. This dimer was twice more subjected (at the end of t_2) to the same two steps, to yield the corresponding dimerization products α -4T and α -8T consecutively. Each cycle of the two steps used half an equivalent of each reactant from

the previous cycle. The one-pot 8T to α -8T conversion (entry 4) was performed in an impressively short reaction time of 90 min. Similarly, relatively high yields of α -4T and α -8T were obtained in the one-pot 4T \rightarrow α -4T (entry 3) and α -2T \rightarrow α -8T (entry 6) conversions, respectively.

Trace amounts of α -6T (2–3%) were isolated from the reaction mixtures of each of the 8T \rightarrow α -8T (entry 4) and the 4 α -2T \rightarrow α -8T (entry 6) conversions. No α -6T was detected in that of the 4T \rightarrow α -4T (entry 3) conversion. The trimer α -3T was not detected in any of the reactions outlined in Table 1. α -6T could have been formed in the 2 α -3T \rightarrow α -6T and in the α -2T + α -4T \rightarrow α -6T coupling reactions.

Two coupling reactions (eqs 3 and 4) were carried out (under competition conditions) to verify at which phase of the one-pot stepwise 8T \rightarrow α -8T and 4 α -2T \rightarrow α -8T conversions the α -6T was formed:



(a) Hg(TFA)₂ (1 equiv.); (b) PdCl₂ (1 equiv.), Et₃N (3 equiv.)

None of α -3T and α -4T were detected in reaction 3. The lack of formation of α -6T excludes the formation of α -6T in a 2 α -3T \rightarrow α -6T coupling pathway in the 8T \rightarrow α -8T synthesis.

On the basis of the results obtained it might be reasonably concluded that formation of α -6T in the 8T \rightarrow α -8T conversion occurred only in the 2 α -4T \rightarrow α -8T coupling phase, and only in the presence of small amounts of α -2T.

The results of the present research reflect an essential conceptual element with regard to the feasibility of the present novel one-pot stepwise synthesis of oligo- α -thiophenes, namely, the reactivity of α - n T decreases (significantly) with increase of n . The above outlined formation of α -6T (and not of α -3T) suggests that the difference in reactivity between α - n T and α -($n+1$)T or α -($n+2$)T decreases with increase of n .

In conclusion, the feasibility of a conceptually novel approach for the one-pot synthesis of oligo(α -thiophenes) from the monomers (thiophene and α -2T) has been demonstrated. This approach consists of performing sequentially the required number of cycles of two reactions, namely, monofunctionalization of the α - n T ($n=1, 2, 4$) and coupling of the product of this reaction.

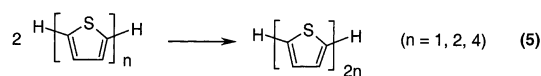
It is our opinion that the present one-pot synthesis of oligo(α -T), as well as the previous one-pot synthesis of oligo-PPV analogues (having extended π -conjugation in the repeat unit),¹⁰ represents a general concept that may be applicable to a one-pot synthesis of conjugated oligomers from the corresponding symmetrical difunctional conjugated monomers. Such oligomerizations may be achievable provided that compatible monofunctionalization and subsequent coupling reactions can be elucidated for a specific monomer of this type.

Experimental Section

General. Thiophene (Aldrich, 99%) and 2,2'-bithiophene (Aldrich, 97%) were used as purchased. Benzene (AR) was dried over sodium wire and distilled from this mixture before use. Triethylamine was kept over sodium hydroxide and distilled from this mixture before use. PdCl₂ (Merck, 99%) and mercuric trifluoroacetate (Merck, 98%) were dried in a vacuum for 12 h before use.

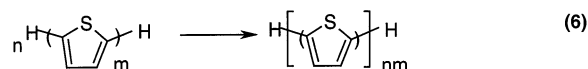
The reaction setup consisted of a 50-mL flask fitted with a self-sealing rubber septum, equipped with magnetic stirring and a dry nitrogen inlet. Liquid materials were introduced into the reaction flask with a hypodermic syringe. All glass parts, syringes, and needles were thoroughly dried at 130 °C and assembled while warm. Reaction products were purified by flash column chromatography with H-60 type silica (Merck).

General Procedure for the One-Pot Dimerization of Oligo(α -thiophenes) (Equation 5). A benzene solution (5–8 mL) of the oligo(α -thiophene) (1 mmol) was cooled to 0 °C. An equivalent amount of mercuric trifluoroacetate was added to this solution. The reaction mixture was stirred for 15 min (t_1) at 0



°C. One equivalent of PdCl₂ and 3 equiv of triethylamine were then introduced to the reaction mixture, which was stirred for a further 15 min (t_2) at 0 °C. Methylene chloride, carbon black, and water were added to the reaction mixture and the mixture was filtered. The aqueous layer was separated and extracted with methylene chloride, the organic layers were combined, dried over anhydrous MgSO₄, and filtered, and the solvent was removed from the filtrate. The residue was subjected to column chromatography on silica gel to yield the corresponding pure dimerization product. The highly insoluble α -8T was purified as described below and not by column chromatography.

General Procedure for the One-Pot synthesis of Oligo(α -thiophenes) from the Corresponding Monomers (Equation 6). The general procedure below was applied for the



following pairs of n and m values: 4, 1; 8, 1; and 4, 2.

A solution of the monomer (0.5 mmol) was dissolved in benzene (8 mL) and cooled to a temperature of 0 °C, which was maintained throughout the whole synthesis. One equivalent of mercuric trifluoroacetate was added to the solution and the mixture was stirred for 15 min (t_1). Palladium chloride (1 equiv) and triethylamine (3 equiv) were then added and stirring was continued for 15 min (t_2). A second portion of mercuric trifluoroacetate (0.5 equiv) was added and the reaction mixture was stirred for 15 min (t_1). Palladium chloride (0.5 equiv) and triethylamine (1.5 equiv) were then added and stirring was continued for a further 15 min (t_2). If needed, a third addition of Hg(TFA)₂ (0.25 equiv), PdCl₂ (0.25 equiv), and Et₃N (0.75 equiv) was performed by using the same experimental conditions as described above. Workup of the reaction mixture was performed, as described above in the general procedure for the one-pot dimerization of oligo- α T. The octamer α -8T obtained (Table 1, entries 4 and 6) contained trace amounts of α -6T, which was removed from the α -8T by applying a workup protocol reported in the literature.¹³

The structures of the oligomers α -2T,^{6a} α -4T,^{6a} and α -8T,⁴ which were determined on the basis of their ¹H NMR and mass spectral data, were found to be identical with the corresponding literature-reported data.

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