

Electrochemical Synthesis of Conducting Polymers from Oligomers Containing Thiophene and Furan Rings

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Synopsis

Oligomers containing 2,5-thienylene and 2,5-furanylene units were synthesized by NiCl_2 (dppp) (dppp = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) coupling of Grignard compounds with the appropriate bromothiophene or bromofuran; UV and electrochemical data are given and discussed in terms of number and kind of heterolene units in the oligomeric species.

INTRODUCTION

Electrically conducting polymers have attracted a great deal of attention in the last few years.¹ As an extension of our previous work on synthesis and electropolymerization of oligo-2,5-thienylenes and oligo-3-substituted-2,5-thienylenes,² the present investigation reflects our interest towards the synthesis of oligomers containing 2,5-thienylene as well as 2,5-furanylene units, their electrochemical properties, and their polymerization. The spectral properties and oxidation potentials of the described monomers and the derived polymeric films are listed in Tables I and II.


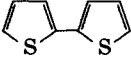
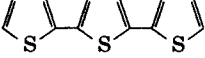
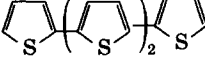
The syntheses of such compounds as reported earlier are rather cumbersome.^{3,4} Recently, the synthesis of a few of such compounds, including the oligomers listed in Table II, was achieved by a Pd-catalyzed coupling reaction between a 2,5-dibromofuran and 2-bromofuran with an appropriate Grignard compound.⁵ We found, according to a method first introduced by Kumuda et al.,⁶ and applied by us for the synthesis of oligomeric thiophenes,² that a NiCl_2 (dppp) catalyzed cross-coupling reaction of the appropriate thiophene-derived Grignard compound and 2-bromosubstituted heterocycles gave such mixed oligomers with reasonable yield without the need to employ the costly Pd-catalyst (Scheme 1).

RESULTS AND DISCUSSIONS

The goal of the synthesis of oligomers containing the mixed units of 2,5-thienylene and 2,5-furanylene was to investigate the possibility to use them to prepare electrochemically conducting polymers to determine the oxidation potentials for both starting monomeric compounds and polymeric

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TABLE I
 UV Spectra and Oxidation Potentials of Thiophene Oligomers

Compound ^a	λ_{\max} CHCl ₃ (nm)	E_{ox}^b (monomer) (V)	E_{Pa} (monomer) (V)	E_{Pa}^d (polymer) (V)
	231 ^c	1.70	2.07	0.95
	302	1.15	1.63	1.00
	355	0.95	1.05	1.04
	390	0.89	0.95	0.93


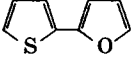
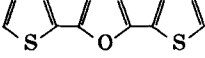
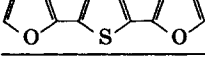
^aAll compounds had bp or mp agreeing with literature values or gave elemental analyses values within 0.4% of theory as well as IR and ¹H-NMR spectra which agreed with the assigned structures.

^bAs obtained from the current-voltage (*i*-*V*) curve during the potentiodynamic synthesis of the compound, by extrapolating the linear part of the curve to the potential axis. Values reported in references to Ag/AgCl electrode.

^cData from Reference 10.

^dPolymer film oxidation potential determinations were conducted in a monomer-free electrolyte.

 TABLE II
 UV Spectra and Oxidation Potentials of Mixed Oligo Heteroarylenes

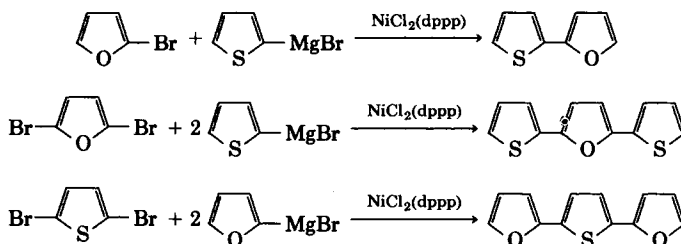
Compound ^a	λ_{\max} CHCl ₃ (nm)	E_{ox}^b (monomer) (V)	E_{Pa} (monomer) (V)	E_{Pa}^d (polymer) (V)
	207 ^c	1.55	1.76	1.07
	268	1.05	1.60	0.80
	315	0.87	1.00	0.98
	312	0.81	0.96	0.80

^aAll compounds gave checking elemental analyses within 0.4% of theory and ¹H-NMR spectra are in agreement with the assigned structures.

^bSee Table I.

^cData from Reference 10.

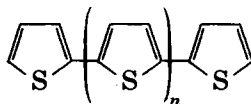
^dPolymer film oxidation potential determinations were conducted in a monomer free electrolyte.



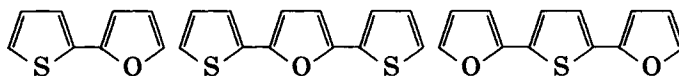
Scheme 1.

films, and to study the effect of introduction of an oxygen heteroatom in the ring on both spectral and electrochemical data. It is evident from the data in Tables I and II that the trend for the oxidation potential values, E_{ox} , is in contrast to what has been reported earlier.⁷ In some previous studies it has been shown⁷ for the case of furan and thiophene that the higher electronegativity of the heteroatom—oxygen versus sulfur—resulted in more positive E_{ox} values. However, by these authors, this relationship did not hold for pyrrole and thiophene—N versus S.^{7,8} Though our data seems to indicate that the furan—thiophene containing oligomers have lower E_{ox} values than the oligomers which have only thiophene units, we are at this point, however, in no position to state that this difference is due to electronegativities of the ring heteroatoms or the kinetics of the polymerization processes as both of these parameters will contribute to the magnitude of E_{ox} . Moreover, a similar trend is also observed for the analogous oligomeric compounds, namely 2,2'-bithienyl and 2-(2-thienyl)furan, 2,2':5',2''-terthienyl, 2,5-bis(2-thienyl)furan, and 2,5-bis(2-furyl)thiophene. These data show unexpectedly that the oxidation of the oxygen containing oligomeric heterolenes proceeds at less positive potentials compared to the corresponding sulfur containing oligomers. From the data obtained so far, it seems as if E_{ox} decreases with increasing numbers of 2,5-furanylene moieties in the monomer.

The extent of the Π -electron cloud of oligomeric compounds of type 1 and type 2 obviously depends only on n . In type 2 oligomers the Π -cloud additionally is influenced by the difference of electronegativities of the heteroatoms in the oligomer.



Type 1

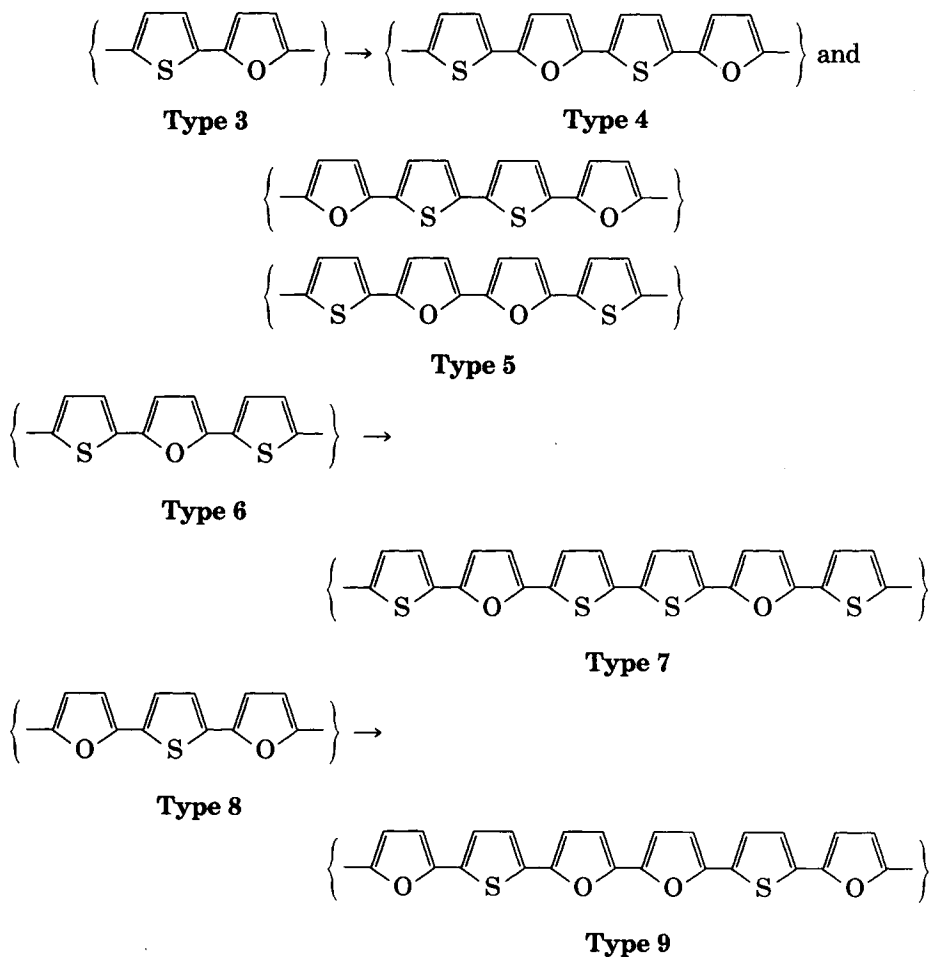


Type 2

The foregoing electronic effects should influence the UV spectral as well as the

electrochemical oxidation potential data. These assumptions are in good agreement with the preliminary results shown in Tables I and II.

Referring to the data in Tables I and II, the λ_{\max} values increase similarly as those reported earlier for oligo-*p*-phenylenes.⁹ The increasing length of the conjugated system and the concomitant enhancement of delocalization possibilities of the derived radical cations will lower the oxidation potential values because the stability of the resulting cation radical depends on the magnitude of electron delocalization. Also, the number and sequence of furan and thiophene moieties containing heterolene oligomers should influence both of the studied parameters. Inspection of Table II reveals that this is the case. The electropolymerization of an oligomer of type 3 could yield an ordered polymer 4 which has alternating furan and thiophene moieties. It also could yield by "head-to-head," "head-to-tail," and "tail-to-tail" polymerization a polymer in which structural units of type 5 are randomly distributed. The only possibility for oligomers of type 6 or 8 to combine is to yield polymers 7 or 9 respectively having repeating units with different sulfur and oxygen alternation. The preliminary results obtained from polymer film's elemental analysis prove the oxygen incorporation in the chain, thus indicating that furan units are part of the polymer.



It is to be mentioned that thin films of these polymers display electroactive and electrochromic properties. All compounds gave adherent films upon electropolymerization. Moreover, the oxidation potential values of polymer films do not correlate with those obtained for starting oligomers. Our hypothesis that with increasing number of rings in the monomers the λ_{\max} of the UV spectra should increase while the values for the corresponding values for E_{ox} should decrease, seems to be a valid one as the data in Tables I and II indicate.²

In summary, we proved for the first time the possibility of obtaining polymeric films upon electrosynthesis of oligomers containing 2,5-thienylene and 2,5-furanylene units. We also show for the first time the relationship between the value of the long-wavelength UV absorption and the oxidation potentials of furan and thiophene rings containing mixed oligomeric heterolenes.

EXPERIMENTAL

Typical procedure for the preparation of an oligomer containing 2,5-thienylene as well as 2,5-furanylene units by a NiCl_2 (dppp) catalysis follows. 2,5-Bis(2-furyl)thiophene: A solution of 2,5-dibromothiophene (0.0045 mol) and NiCl_2 (dppp) (60 mg) in ether was added dropwise to an ether solution of 2-furylmagnesium bromide (0.1 mol). After refluxing for 20 h the mixture was hydrolyzed with 1.25M aqueous HCl, the ether layer separated, and the aqueous solution extracted exhaustively with ether. After drying over MgSO_4 , the solution was concentrated *in vacuo* and the remaining oil was purified over a chromatographic column (using hexane) to give 0.53 g (55%) of a greyish green liquid, bp 67–69°C.

Electrochemical polymerizations were carried out with a three electrode system where the working electrode was a platinum disc electrode having a surface area of 0.3 cm² model MF2013 from Bioanalytical Systems, Inc. (BAS). All the potentials in the polymerization and voltammetric studies were referenced to an Ag/AgCl electrode (3M KCl). The auxiliary electrode was a 2 × 2 cm² platinum sheet. HPLC grade acetonitrile from Fisher Scientific Co. was kept over 3Å type molecular sieves for at least 24 h prior to the experiments. During the polymerizations a monomer concentration of 0.050M in acetonitrile with 0.050M tetrabutylammonium tetrafluoroborate (TBATFB) as supporting electrolyte (Aldrich Chemical Co.) was used. Polymer films were grown on the platinum surface galvanostatically with an optimized current density of 2 mA/cm² for 30 s, using a PAR Model 173 Potentiostat/Galvanostat mounted with a PAR Model 176 current-to-voltage converter.

Voltammetric studies were performed in monomer free solutions of acetonitrile containing 0.050M TBATFB with the same 3-electrode system described above. The cyclic voltammetry unit (BAS) was a model CV-1B and a Hewlett-Packard Model 7004B x-y recorder. All the cyclic voltammograms were recorded with a scan rate of 50 mV/s. The electrochemical preparations and measurements were carried out under Ar atmosphere with the solutions degassed by Ar bubbling. All reported E_{ox} values were reproducible within ± 10 mV.

The physical and chemical properties of the resulting polymers, and the cyclic voltammograms for the monomers are not completely free from the

effects of polymer formation. Our research reveals that furan has a lower oxidation potential than thiophene under the conditions reported here.

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