Synthesis of Oligomeric 2,5-Thienylenes; Their U.V. Spectra and Oxidation Potentials

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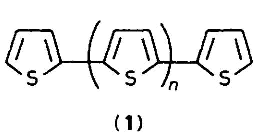
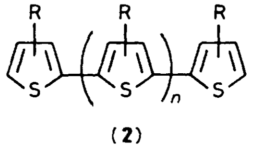
Oligomeric 2,5-thienylenes and 3-methyl-2,5-thienylenes have been synthesized by $NiCl_2$(dppp) (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) coupling of Grignard compounds with the appropriate bromothiophene; u.v. spectra and oxidation potentials of the oligomers are dicussed in terms of coplanarity of the oligomeric species.

In continuation of our investigations of thiophene based polymers which become conducting only after immersion in water,[1] we extended our efforts towards the synthesis and polymerization of oligo-2,5-thienylenes and oligo-3-substituted-2,5-thienylenes. A recent publication in which, among others, the synthesis and polymerization of 2,2′-bithienylene is reported[2] prompts us to publish our first results in this area. The oligomeric-2,5-thienylenes which we studied have the general structures (**1**) and (**2**).

A number of compounds of type (**1**) were already known but were prepared by rather cumbersome methods and obtained in a pure state, if at all, after lengthy and high-loss work-up procedures.[3a—g] Compounds of type (**1**) and type (**2**) can be obtained conveniently by a $NiCl_2$(dppp) (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) catalysed cross-coupling reaction of a 2-bromothiophene with an appropriately substituted thiophene-derived Grignard compound according to a method first introduced by Kumada *et al.*[4] and recently used by us and

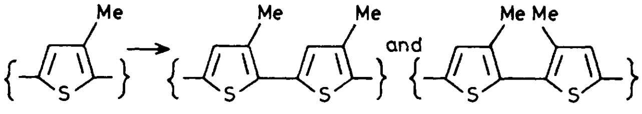


(1)

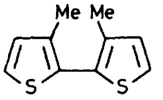


(2)

n = 0, 1, 2, 3, 4; R = Me in various positions



(3) (4)



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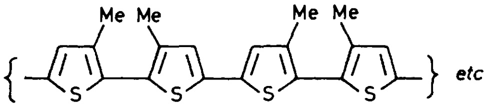

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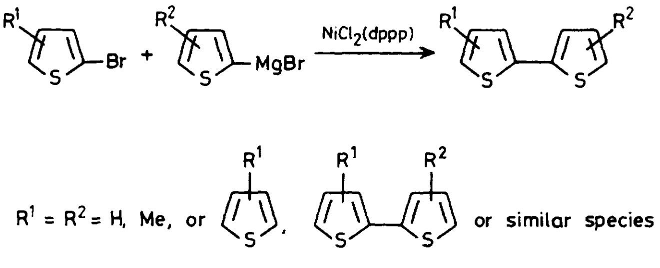


Scheme 1

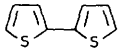
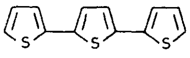
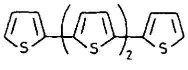
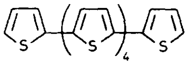
others for the preparation of 3-substituted alkyl-[5] and aryl-thiophenes (Scheme 1).†[5–7] Kagan has also used this method recently for obtaining various isomeric terthienyls.[8]

Compounds of types (**1**) and (**2**) were synthesized in order to study in more depth electrochemical properties of 2,5-thienylene-based polymers with the eventual goal of optimizing the conductivity of our 'water-dopable' poly(3-substituted-2,5-thienylenes).[9] By starting the polymerization with larger monomeric blocks, we hoped to obtain a polymer with less random distribution of the methyl groups, *e.g.* facing each other or not. Thus, in further polymerization, unit (**3**) could combine with itself or with unit (**4**) *etc.* The result would be a rather unordered polymer. However, if the monomer were, *e.g.*, 3,3′-dimethyl-2,2′-bithienyl (**5**) polymerization should give units such as (**6**), resulting in a much more ordered polymeric material. Also, with a lower degree of random distribution coplanarity of the polymers might be effected which would have a marked influence on the u.v. maxima.

The extent of the π-electron cloud of type (**1**) oligomers depends only on *n*, whereas in type (**2**) oligomers steric hindrance due to the methyl groups should influence coplanarity and thus overlap of π-electrons. This effect should have an influence on the u.v. spectra and the oxidation potential of the oligomers as well. Our preliminary results (Tables 1 and 2) confirm this assumption.

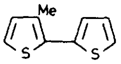
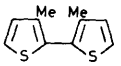
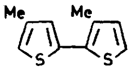
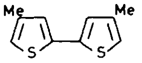
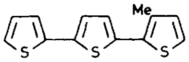
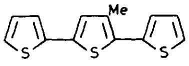
As is evident from the data in Table 1 the $\lambda_{max.}$ values increase in a similar manner to that shown earlier for oligo-*p*-phenylenes.[11] With increasing *n* the $\lambda_{max.}$ increment between adjacent compounds decreases, indicating a lessening degree of overlap due to increasing thermal motion. The

Table 1.

Compound[a]	$\lambda_{max.}$/nm, CHCl$_3$	E_{ox}/V
	302	1.28
	355	1.05
	390	0.97
	432	0.46

[a] All compounds had b.p.s or m.p.s agreeing with literature values or gave elemental analyses values within 0.4% of theory as well as i.r. and ^{1}H n.m.r. spectra which agreed with the assigned structures. E_{ox} is taken as the potential of the peak oxidation current of the cyclic voltammograms (scan rate 50 mV s^{-1}). Although the electro-oxidation is irreversible, the mechanism and rate constants would eventually be the same for all the oligomers. Hence, the potential of the peak oxidation currents obtained from the cyclic voltammograms should correlate directly with the formal potential, E^{o1}, for the redox reaction.[10]

Table 2.[a]

Compound	$\lambda_{max.}$/nm, CHCl$_3$	E_{ox}/V
	299	1.22
	270	1.58
	302	1.07
	312	1.16
	352	1.13
	336	1.11

[a] All compounds gave checking elemental analyses within 0.4% of theory and ^{1}H n.m.r. spectra are in agreement with the assigned structures.

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† The preparation of 2,2′:5′,2″-terthienyl is typical. A solution of 2,5-dibromothiophene (0.4 mol) and NiCl$_2$(dppp) (60 mg) in ether was added dropwise to an ether solution of 2-thienylmagnesium bromide (0.1 mol). After refluxing for 16 h the mixture was hydrolysed with 1M aqueous HCl, the ether layer separated, and the aqueous solution extracted exhaustively with ether. After drying over MgSO$_4$ the solvent was evaporated and the remaining solid was recrystallized from hexane to give 8.5 g (86%) of slightly greenish crystals; m.p. 94—95 °C (lit.[3b] 95 °C); *m/z* 248 (*M*$^+$).

increasing length of the conjugated system and thus the increase in delocalization possibilities for the derived radical cations manifests itself by decreasing values for the oxidation potentials. Thus, the larger *n* becomes, the more stable the derived cation is and consequently a lower oxidation potential is observed.

The relationship between the position of $\lambda_{max.}$ and E_{ox} is not clear cut with the methyl substituted oligo-2,5-thienylenes, because decreasing overlap caused by steric hindrance imposed on the molecule by the methyl groups and the $+I$ effect of the latter influence delocalization possibilities and thus the stability of the derived radical cation in ways which are difficult to predict.

Finally, the morphology of the electro-oxidatively obtained polymers depends strongly on the value for *n* as well as on the position of the methyl groups.

In summary, we have synthesized in a reproducible and convenient way oligomeric 2,5-thienylenes and 3-methyl-2,5-thienylenes and shown for the first time that there exists a close relationship between the position of the long-wavelength u.v. absorption and the oxidation potentials of these compounds.

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