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Citation for published version (APA):
Havinga, E. E., Rotte, I., Meijer, E. W., Hoeve, ten, W., & Wynberg, H. (1991). Spectra and electrical properties of soluble partially alkyl-substituted oligomers of thiophene up to 11 rings. *Synthetic Metals*, *41*(1-2), 473-478. https://doi.org/10.1016/0379-6779(91)91110-V

DOI:
10.1016/0379-6779(91)91110-V

Document status and date:
Published: 01/01/1991

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Synthetic Metals, 41–43 (1991) 473–478

SPECTRA AND ELECTRICAL PROPERTIES OF SOLUBLE PARTIALLY ALKYL-SUBSTITUTED OLIGOMERS OF THIOPHENE UP TO 11 RINGS

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Abstract

A series of strictly α,α'-coupled oligomers of thiophene containing 3,4,5,6,7,9, and 11 rings and provided with 0 to 5 side groups (*n*-butyl, *n* -dodecyl or *tert*-butyl) have been prepared and their melting points, solubilities in chloroform, UV-vis absorption and emission spectra of both solutions and solids, and conductivities after doping with iodine have been measured. The dependence of the conjugation length on the number of rings, and on the number, length, and position of side groups is discussed.

Introduction

The concept of conjugation length plays an important role in the theories of the conductivity and the non-linear optical properties of conjugated polymers. Reliable experimental data on this subject are, however, very scarce. The modification of conjugated polymers with flexible side chains in order to improve their tractability has become wide-spread, but the influence of such a modification on the conjugation length remains rather uncertain [1,2] . In order to study the interrelation between chemical structure and various physical properties in such polymers we have prepared a series of partially alkyl-substituted oligothiophenes as a model system.

The series includes 3,4,5,6,7,9 and 11 α,α' -coupled thiophene rings. Up to three rings are substituted at their β-position with a *n*-butyl (*b*) or *n*-dodecyl (*d*) group. Furthermore, two oligomers carrying *tert*-butyl (*t*) end groups at the α-positions were synthesized. The method of synthesis, *via* the Stetter reaction to 1,4-diketones, followed by ring closure with Lawesson's reagent, leaves no doubt about the α,α'-coupling of the thiophene moieties and the characterization with ^{1}H-NMR and IR spectra agrees with the structures assigned. These results will be published elsewhere [3]. The synthesis leads, in general, to a mixture of isomers differing only in the position of the *n* -alkyl groups in a certain

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ring. In Table 1 the number of isomers for all oligomers studied is listed. The oligomers are denoted by a short-hand notation illustrated in Fig. 1.

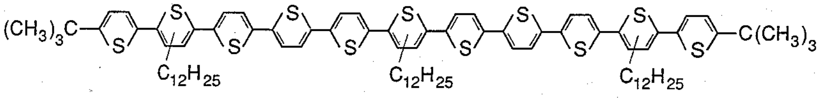

Fig. 1. Penta-substituted oligomer having 11 α,α'-coupled rings. The short-hand notation reads T_{11} d_3(2,6,10) t_2(1,11), meaning 11 thiophene rings (T_{11}), three dodecyl groups (d_3) at rings #(2,6,10) and two *tert* -butyl groups (t_2) at rings #(1,11)

In this paper we report on the X-ray structural data, melting points and solubility in $CHCl_3$, optical UV-vis absorption and emission spectra, and conductivity after doping with iodine. The results are discussed in relation with the conjugation length in these oligomers.

Experimental

Spectra were recorded with the aid of a Philips X-ray automatic diffraction unit PW 1730 using Cu$K\alpha$ radiation, starting with $\theta = 2°$, a Varian Superscan 3 UV-vis spectrometer, a Perkin Elmer LS-50 luminescence spectrometer and a Bruker IFS 45 FTIR spectrometer, respectively. Melting points were determined in a hot-stage microscope. Solubility data were obtained by comparing the maximum absorbance of a standard solution of the oligomer in $CHCl_3$ (Merck, *pa*) with that of a saturated solution, assuming the validity of Beer's law.

Conductivities were measured using a four-probe method on two different types of samples, *viz*. bars (20 x 5 x ~ 0.5 mm^3) pressed at 700 MPa and thin coherent layers (25 x 5 x 0.1 mm^3 approx.) made by melting the compound on a ceramic plate. Iodine-doped samples were obtained by heating the samples at 80 °C overnight in a closed vessel saturated with iodine, followed by cooling to room temperature in the vessel.

X-ray results, melting and solubility.

In Table 1 a compilation of physical data measured on the series of oligomers is given. It is seen that crystallinity decreases gradually with increasing length of the oligomers, ending at (nearly) completely X-ray amorphous compounds. The melting point increases with increasing length of the conjugated oligothiophene, and decreases progressively by increasing number and/or length of alkyl side groups. The solubility in $CHCl_3$ follows the opposite pattern. These trends are in keeping with the notion that the π -electron system has a large polarizability increasing with length, that contributes more to the Vanderwaals interaction energy between the molecules than alkyl groups. Steric constraints in packing of substituted oligomers may be another important factor. The T_{11} b_3(4,6,8) shows a larger influence of the butyl groups on the melting point and solubility than the corresponding T_{11} b_3(2,6,10). A simple explanation, which also fits the other data (see below) on these compounds is that next-nearest neighbour chains cause additional twisting of the main chain. The *tert*-butyl end groups seem to have only a minor influence.

TABLE 1. Number of isomers (N), X-ray results*, hot-stage melting point (T_m), solubility (c_{max}) and wavelength of maximum absorption (λ_{max}) in $CHCl_3$.

N	Compound	X-ray*	T_m (°C)	c_{max} (g/l)	λ_{max} (nm)
1	T_3	c	93-95		354
1	$T_3\ d(2)$	c	39-40		345
1	T_4	c	193-195	3.5	394
1	T_5	c	252-258	0.2	415
2	$T_5\ b(2)$	c	125-126	50	412
2	$T_5\ d(2)$	mc + a	76-78	120	407
3	$T_6\ d_2(2,5)$	c + a	80-84	100	423
1	$T_7\ t_2(1,7)$	c	340	<0.05	451
3	$T_7\ b_2(2,6)$	c	132-134	20	440
1	$T_7\ d(4)$	c	160-162	2.1	435
2	$T_9\ d(4)$	mc	193-195	1.6	455
4	$T_{11}\ b_3(4,6,8)$	a + (mc)	119-125	10	441
4	$T_{11}\ b_3(2,6,10)$	a + (mc)	170-173	2	458
4	$T_{11}\ d_2(2,10)\ b(6)$	a + (mc)	150-161		462
4	$T_{11}\ d_3(2,6,10)$	a + mc	140-142	2.3	462
4	$T_{11}\ d_3(2,6,10)\ t_2(1,11)$	a	117-122	2.6	463

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* c = crystalline, mc = microcrystalline, a = amorphous, ( ) = trace.

Absorption and Emission spectra.

The absorption spectra of the compounds in $CHCl_3$ -solution all show a single broad band, whose maximum shifts towards longer wavelengths with increasing length of the molecules (see Table 1). The emission spectrum consists of 2 bands and a shoulder, independent of the wave length of excitation as long as it is within the absorption band. A characteristic example is given in Fig. 2a. The emission spectra are very similar to those of poly(3-hexylthiophene) [5], indicating that the emitting excitations (neutral bipolarons?) in the oligomers and polymer are similar too.

From the λ_{max} data in Table 1 it is seen that side groups cause a slight shift to lower wavelengths, and that next-nearest ring substituents have a larger influence than substituents further apart. Comparing this with data of poly(3-hexylthiophene) ($\lambda_{max} \sim 435$ nm [2,4]) and poly(3,3′-dihexyl-2,2′-bithiophene) ($\lambda_{max} = 389$ nm [1]) shows that the cooperative effect on the decrease of λ_{max} (and, hence, the conjugation length) is more pronounced the closer the side groups approach each other. Supporting evidence for this interpretation follows from the values of the molar extinction coefficients ε per thiophene ring , *viz.*$T_{11}b_3(2,6,10)$ 8700 l mol^{-1} cm^{-1}, and $T_{11}\ b_3(4,6,8)$ 5300 l mol^{-1} cm^{-1}.

Recent results the third order non-linear optical suceptibility γ of some of these oligomers [6] show that for this NLO property a saturation of the conjugation effects sets in around n = 7. From the present optical data we conclude, however, that even for n = 11 no complete saturation occurs. This discrepancy may be due to a less planar confuguration in dilute PMMA solutions (NLO-measurements) than in chloroform solutions, because in the latter case λ_{max} for n = 9 and 11 is some 10 nm higher.

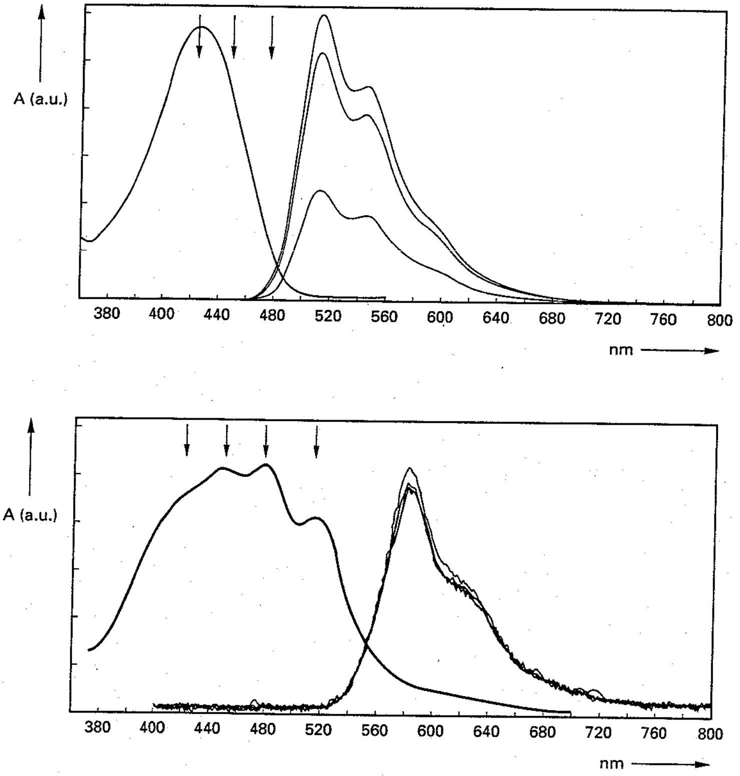

Fig. 2. Absorption and emission spectra of $T_6\ d_2(2,5)$in $CHCl_3$-solution (a) and as a solid film (b). The excitation wavelengths are indicated by arrows.

Solid-state absorption spectra were measured on thin films obtained by evaporating chloroform solutions or spin-coating chlorobenzene solutions of the oligomers. In general the medians of the absorption of solid films lie at higher wavelengths than those of the solutions. The lower oligomers show side peaks or shoulders at higher wavelengths, just as found in unsubstituted oligothiophenes [7] and poly(3-alkylthiophenes) [8]. In the absorption spectra of solid films of the higher oligomers, especially those bearing dodecyl side chains, clear-cut main peaks can no longer be discerned. The emission spectra, on the other hand, are very similar to those from the oligomer solutions in chloroform, except for a shift up to 0.3 eV to lower energies, and the low energy shoulder is missing or less clear. Fig. 2b shows as an example the absorption and emission spectra of $T_6\ b_2(2,5)$.

A detailed explanation of the solid film absorption spectra cannot be given. It is worth noting that spectra of the oligomers in diluted solid solutions (a few %) in PMMA are very similar. However, at very high dilution the spectra in PMMA become similar to the chloroform solution habitat. This means that the multimaxima spectra are probably due to aggregates or small crystals. Even so an interpretation as solely being due to phonons (vibrational side bands) seems to us to be unlikely because of the very high intensity and large number of maxima. A mixture of various conformers that differ in the number of transoid and cisoid ringconnections may be a better proposal.

Conductivity

The conductivities of a number of the thiophene oligomeres after doping with iodine are given in Table 2. For all samples we checked afterwards whether or not post-polymerization had taken place during the doping process by measuring IR spectra (ratio of C-H out-of-plane peaks at 687 and 792 cm^{-1}) and visible absorption spectra of chloroform solutions (shift of the absorption maximum to longer wavelengths). Such post-polymerization during doping has been found in the AsF_5-dope of polyphenylenes [9].

TABLE 2. Specific conductivities, σ (S/cm), for various oligomers doped until saturation at room temperature with iodine. Values in parentheses refer to samples in which post-polymerization during doping was detected.

Compound	compacted powder	fused bar
T_4	(2)	(2)
T_5		(3)
$T_5\,b(2)$	0.04	0.01
$T_5\,d(2)$	(1)	
$T_6\,d_2(2,5)$		(3)
$T_7\,t_2(1,7)$	0.02	0.05
$T_7\,b_2(2,6)$		0.2
$T_7\,d(4)$	2	
$T_{11}\,d_3(2,6,10)$	6	20
$T_{11}\,d_3(2,6,10)\,t_2(1,11)$	6	

It can be seen that for a number of lower oligomers, including all non-substituted ones, we find high conductivities connected with post-polymerization (data given in parentheses). For the other oligomers no trace of post-polymerization could be detected. In two oligomers the α-placed *tert*-butyl groups block the possibility of α-α′-coupling completely. The doped oligomers are X-ray amorphous, which makes a comparison more meaningful than in the case of unsubstituted polyphenylenes [10].

The data show that the conductivity of thiophene oligomers increases with length (or with conjugation length). The higher coherence of the molten layers accounts for the higher conductivities as compared with compacted powders. The conductivity of the T_{11} oligomers approaches that of the alkyl substituted-polythiophenes, 10 to 100 S/cm.

Our data for T_4 and T_5, whose oligomers were clearly post-polymerized during doping, are about the same as those given by Cao *et al*[11]. These authors, however, claim that their samples were not post-polymerized during doping. Our results are clearly at variance with this claim, and the fact that the conductivities of oligomers in which post-polymerization is absent, such as $T_5\ b(2)$ and $T_7\ t_2(1,7)$, are about two orders of magnitude lower than that of T_5 agrees with post-polymerization in the latter case. It may be remarked that even at low concentration of post-polymerized material the conductivity will be much increased.

Conclusions

In partially substituted oligomers of thiophene the conjugation length measured by the UV-vis absorption spectra of solutions in chloroform increases with the length of the π-electron system. At 11 α, α' -coupled thiophene moieties saturation is approached, but not reached. Alkyl substituents at β -positions decrease the conjugation length slightly, with a greater influence of longer alkyl groups. Neighbouring alkyl groups such as in poly(alkylthiophenes) cooperate in this reduction and even for next-nearest substituents an enhanced effect is found.

The solid-state absorption spectra are very complicated, consisting of 3 to 5 peaks of sometimes comparable intensities, and point to a greater conjugation length in the solid state as compared with the chloroform solutions. Again no saturation can be found. This is corroborated by the steady increase of conductivity of iodine doped samples with increasing length, up to 20 S/cm.

The solubility, melting points and degree of crystallinity all fit in with the notion that side groups tend to destroy planarity and agree with the rules about conjugation length given above.

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