

Electrochemical synthesis of new electroactive polymers from dithienylene-vinylene derivatives

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Abstract

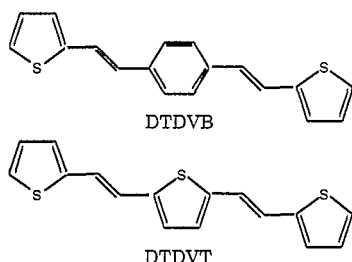
Highly conjugated thiophene derivatives, based on thienylene-vinylene and thienylene-vinylene-phenylene units, have been synthesized in order to examine: (i) the effect of such regular conjugated monomer structures on the polymerization; (ii) the optical and electrochemical properties of the corresponding conjugated polymers. The all-trans monomers have been prepared by a Wittig reaction and the polymers have then been synthesized electrochemically. The polymers are electrochromic and can be reversibly doped both oxidatively and reductively. Their electrochemical behavior and optical properties have been analysed on the basis of quantum-chemical calculations.

Keywords: Electrochemical synthesis; Dithienylene-vinylene derivatives

1. Introduction

The electropolymerization of heterocyclic monomers to form redox active polymers is highly dependent on the monomer oxidation potential. Considering short conjugated for electrochemical polymerization has the advantages of decreasing the monomer oxidation potential and predetermining most of the linkages between the heterocyclic entities [1]. Moreover, starting from short oligomers clearly increases the potential for designing the polymer electronic structure because, using organic synthesis, one can combine at will various conjugated building blocks such as vinylene units, phenylene, and thiophene groups. The polymerization of appropriately-designed mixed oligomers therefore appears of particular interest for the control of both the bandgap and the redox potentials in the conjugated polymers.

Following this approach, we report here the synthesis and the electronic properties of two novel conjugated monomers: 2,2'-dithienyl- ω,ω' -1,4-divinyl benzene (DTDVB) and 2,2'-dithienyl- ω,ω' -2,5-divinyl thiophene (DTDVT) (Scheme 1), along with their electrochemical polymerization and the characterization of their electronic properties. We compare the optical absorption and electrochemical data to the electronic structure obtained by quantum-chemical calculations on the monomers and the polymers.



Scheme 1

2. Monomers synthesis

Both monomers were successfully synthesized via a two-step reaction route [2]. Tetraethyl-1,4-phenyl-bis(methylphosphonate) was obtained by the reaction of 1,4-bis(chloromethyl) benzene with triethylphosphite at 120°C (yield = 98%). When reacted with sodium hydride in THF, followed by addition of 2-thiophene carboxaldehyde, this compound was converted into the desired DTDVB in

68% yield. DTDVT was obtained following the same procedure, starting from 2,5-bis-(chloromethyl) thiophene (yield = 42%). The structure of both monomers was confirmed by H-NMR and FT-IR.

3. Results and discussion

3.1. Optical properties of monomers

Figure 1 shows the experimental UV-VIS absorption spectrum of DTDVB compared to the theoretical curve obtained with the Intermediate Neglect of Differential Overlap/Single Configuration Interaction (INDO/SCI) method.

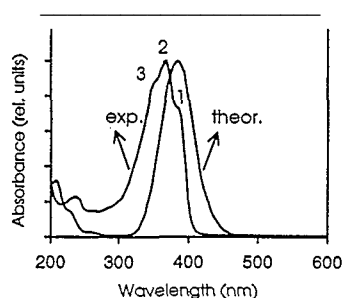


Fig.1 : Experimental and theoretical absorption spectra of DTDVB

An intense peak is observed at low energy, together with several low intensity lines at higher energy, in good quantitative agreement with the theoretical spectrum. The main absorption band is due to an excitation from the highest-occupied molecular orbital to the lowest-unoccupied electronic level, as determined from theoretical data. Experimentally, this peak shows a fine structure which we ascribe to a vibronic structure (and not to a chemically unresolved mixture of cis-trans isomers).

Arguments in favor of this vibronic origin are: first, the Wittig reaction used for the monomer synthesis usually leads to all-trans products, which is confirmed by NMR measurements. Secondly, the energy calculated for the first optical transition of DTDVB isomers is 3.23, 3.49, and 3.64 eV for the all-trans, cis-trans, and all-cis isomers respectively, which is inconsistent with the energy difference between peaks 1-2 and 1-3. Thirdly, the observed splittings agree with the energy of an intense vibrational mode observed at 1179cm^{-1} on the Raman spectrum. Finally, this fine structure is very similar to that observed for the corresponding polyparaphenylene-vinylene oligomers, for which a vibronic origin has been experimentally established and theoretically rationalized [3]. A similar lineshape is observed in the case of DTDVT and we also conclude to a vibronic fine structure for the same reasons.

3.2. Electrochemical polymerization

The cyclic voltammetric scanning electro-polymerization behavior of DTDVT and DTDVB was examined in $\text{CH}_3\text{CN}/0.1\text{M Et}_4\text{NClO}_4$ (TEAP). For comparison, polybithiophene (PBT) was also synthesized in the same conditions. These oxidative polymerizations lead to the formation of electroactive thin films. The DTDVB and DTDVT monomers exhibit significantly lower polymerization potentials than BT, in agreement with the calculated ionization potentials (Table 1). This merely results from the smaller π system of BT, which is accordingly less prone to oxidation than the two thienylene-vinylene molecules. Both experiment and theory show that the oxidation potential is higher for DTDVB compared to DTDVT because the phenylene unit which is more aromatic than the thiophene ring, makes the π -conjugation along the backbone less effective. The doped PDTDVB/ ClO_4 and PDTDVT/ ClO_4 were subsequently cycled between their charged and neutral forms in monomer-free electrolyte. The polymers are electrochromic and can be reversibly doped both oxidatively and reductively in TEAP. A linear increase of the oxidation-peak current with scan rate was found as expected for an electrode-supported electroactive film.

Table 1 : Experimental oxidation potential ($E_{ox}; V$) and theoretical ionization potential ($I_p; eV$) of the monomers and the corresponding polymers, relative to BT and PBT. Bandgaps (eV) of the polymers, as obtained by electrochemical measurements, by optical absorption spectroscopy and from theoretical results, respectively.

	Monomers		Polymers		Polymer bandgap		
	I_p	E_{ox}	I_p	E_{ox}	Elec.	Opt.	Theor.
BT	0	0	0	0	1.85	1.85	1.68
DTDVB	-0.56	-0.12	-0.22	-0.15	1.85	1.87	1.69
DTDVT	-0.77	-0.32	-0.39	-0.25	1.70	1.55	1.37

The oxidation potential for those polymers is smaller than that of PBT, in agreement with the calculated polymer ionization potential (Table 1). This difference cannot be accounted for by differences in the conjugation lengths, as it was the case for the parent monomers, since the three polymers must contain fairly long conjugated segments. The chemical structure of the basic polymer units should rather be invoked. The PDTDVT structure formally corresponds to the insertion of vinylene units in the all-thiophene backbone of PBT, which is known to reduce the oxidation potential. This effect is due to the π -electrons of the vinylene double bond which tend to interact more strongly with the neighboring π system and enhance the electronic delocalization of the frontier levels, resulting in an increase of the width of the upper valence band and thus in a decreased oxidation potential. The enhancement of electronic delocalization is less pronounced in PDTDVB compared to PDTDVT, because the π electrons within the phenylene rings tend to remain more localized than those in the less aromatic thiophene rings. The oxidation potential of PDTDVB is accordingly located between those of PBT and PDTDVT.

3.3. Evolution of the bandgap

The polymer bandgaps have been estimated from the onset of the absorption spectrum in the neutral state, and were found in good agreement with the electrochemical data obtained from the difference between the onset of the anodic oxidation peak (p-doping) and the cathodic reduction peak (n-doping) on the voltamperogram (Table 1). The theoretical values are also consistent with the optical absorption data: very similar bandgaps are calculated for PBT and PDTDVB, significantly higher (0.3 eV) than for PDTDVT. Compared to PBT, only small changes are expected for PDTDVB, since the effects of vinylene units and phenylene rings on the electronic structure tend to cancel each other. In contrast, only vinylene units are at work in PDTDVT and the bandgap significantly decreases with respect to PBT.

4. Synopsis

The Wittig reaction scheme has been used to synthesize two all-trans thienylene-vinylene derivatives. As a first step, the optical and electrochemical properties of these monomers have been rationalized on the basis of quantum-chemical calculations. These monomers have then been polymerized electrochemically; this leads to electroactive compounds that can be both p- and n-doped. The electrochemical properties and absorption spectra of the two polymers have been compared to polybithiophene, from both the experimental and the theoretical point of view. The analysis of the results indicates that phenylene and vinylene units have antagonistic effects on the electronic structure.

5. References

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