The Charge Storage Mechanism of Conducting Polymers: A Voltammetric Study on Defined Soluble Oligomers of the Phenylene–Vinylene Type

Jürgen Heinze,[a]* John Mortensen,[a] Klaus Müllen,[b] and Rainer Schenk[b]

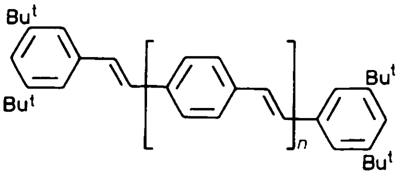
[a] *Institut für Physikalische Chemie der Universität Freiburg, Albertstrasse 21, D-7800 Freiburg, Federal Republic of Germany*

[b] *Institut für Organische Chemie der Universität Mainz, Johann Joachim Becher-Weg 18–20, D-6500 Mainz, Federal Republic of Germany*

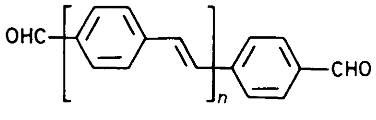
The reductive charging–discharging behaviour of several newly synthesized soluble oligo-*p*-phenylene–vinylenes was studied by cyclic voltammetry; the results show that both the number of redox states and the magnitude of their energetic interaction depend on the chain length of the corresponding oligomer.

Until now, the electrochemical charge storage mechanism of conducting polymers has not been properly understood. Electrochemists have proposed a combination of potential dependent faradaic and capacitive processes to characterize the charging–discharging properties of, *e.g.*, polypyrrole (PPy) or polythiophene (PTh), and a two-step proton-electron transfer mechanism in the case of polyaniline (PANI).[1,2] Among physicists the charge storage mechanism is mainly described in terms of the bipolaron model,[3,4] which ideally assumes the formation of multiple thermodynamic stable di-ion states (= bipolarons) associated with local geometric distortions of the chain. At the moment, the known electrochemical data do not unequivocally correlate with the bipolaron concept. The difficulties in the interpretation of the experimental phenomena result from the fact that polymeric systems, in contrast to monomeric molecules with one or two redox sites, exhibit multi-electron transfer processes with varying interaction energies between the different redox states. Moreover, conducting polymers often possess an irregular structure[5,6] and have a more or less broad molecular weight distribution. To overcome these drawbacks we have now synthesized several soluble oligomers, (**1a**)—(**1d**), of defined structure and chain length, belonging to the *p*-phenylene–vinylene series. The redox behaviour of these systems was studied in tetrahydrofuran (THF)–$NaBPh_4$. The results obtained provide unequivocal evidence for the first time of the character of the charge storage mechanism in such conjugated oligomers.

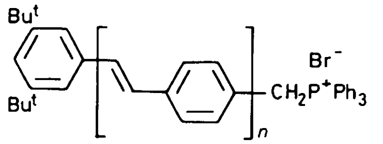
Oligo-*p*-phenylene–vinylenes with higher molecular weight have an extremely low solubility in organic solvents.[7] In our approach towards a homologous series of soluble derivatives we introduced t-butyl substituents.[8] The positions of these substituents in the title compounds (**1**) were chosen in such a way that there was no steric hindrance of the π,π-conjugation along the chain. The method of choice, clearly, is the Wittig reaction.[7,9] Terephthaldialdehyde (**2a**) served as the building block for the synthesis of (**1a**) and (**1c**) (*n* odd), while the synthesis of (**1b**) and (**1d**) (*n* even) started from 4,4′-stilbenedicarbaldehyde (**2b**).[10] Their reaction partners were 3,5-di-t-butylbenzyltriphenylphosphonium bromide (**3a**)[11] and its hitherto unknown homologue (**3b**). For the synthesis of (**3b**) 4-methylbenzaldehyde and (**3a**) were submitted to a Wittig reaction to give 3,5-di-t-butyl-4′-methylstilbene (m.p. 81 °C; yield 57%), which was then converted into the corresponding phosphonium salt. The final chain formation [(**2a**) + (**3a**), (**2b**) + (**3a**), (**2a**) + (**3b**), and (**2b**) + (**3b**); dimethylformamide,



(1) a; n = 1
b; n = 2
c; n = 3
d; n = 4
e; n = 5
f; n = 6



(2) a; n = 0
b; n = 1



(3) a; n = 0
b; n = 1

lithium ethoxide, room temp.] gave (**1a**), (**1b**), (**1c**), and (**1d**) in 39, 58, 33, and 30% yield, respectively.† The solubility of (**1a**)—(**1d**) is significantly higher than that of the corresponding unsubstituted oligo-*p*-phenylene–vinylenes [*e.g.* (**1b**): 23 mg/ml, distyrylstilbene: 2.3 µg/ml ($CHCl_3$; 22 °C)]. This outcome allows for a cyclic voltammetric and e.s.r. spectroscopic[12] study of the redox reactions of (**1a**)—(**1d**). The higher homologues (**1e**) and (**1f**) (n = 5,6) were also prepared; however, they could not be characterized by cyclic voltammetry owing to insufficient solubility.

The cyclic voltammograms (Figure 1) represent reduction experiments within the homologous series of (**1a**)—(**1d**). As high background currents, especially in the case of (**1c**) and (**1d**), disturbed the current–voltage curves all voltammograms were corrected with respect to capacitive currents and electroactive impurities (*e.g.* biphenyl). To avoid additional side reactions the experiments were carried out under super-dry conditions in THF–$NaBPh_4$. The typical ion pairing effects in the presence of alkali-ions were minimized by adding 15-crown-5.

As can be seen from Figure 1, the number of redox steps increases with increasing chain length of the oligomer. While (**1a**) (n = 1) gives rise to a dianion, the homologue (**1d**) (n = 4) is transformed into a stable penta-anion. Three effects are especially significant. (i) The potentials of already existing redox states shift to less negative values when the next higher homologue is reduced. Obviously, the redox energies of different states gradually approach a common convergence limit when the chain length is increased. (ii) The redox states degenerate pairwise with increasing chain length but no 'two-electron' transfers are observed as are predicted for energetically stabilized di-ion states.[4] (iii) Adding successive phenylene–vinylene subunits in the molecular chain enlarges the number of accessible redox states in agreement with

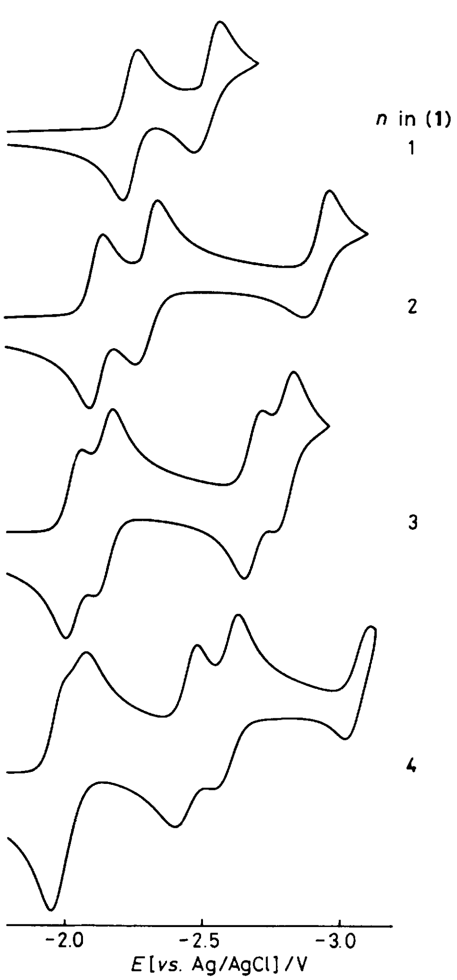


Figure 1. Cyclic voltammograms (corrected for background current) for the reduction of (**1a**)—(**1d**) (v = 100 mV/s) at −40 °C in THF–BPh_4 with 15-crown-5.

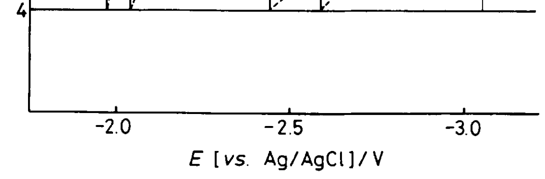


Figure 2. Correlation diagram for the redox states in (**1a**)—(**d**).

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† M.p.: 224—225 °C (**1a**), 260 °C (**1b**), 294 °C (**1c**), 307 °C (**1d**); ^1H n.m.r., *e.g.* (**1c**) ([$^2H_8$] THF; 400 MHz): δ 1.37 (s, 36H), 7.17 (d, 2H, ^3J 16.5 Hz), 7.23 (s, 4H), 7.26 (d, 2H, ^3J 16.5 Hz), 7.37 (t, 2H, ^4J 1.5 Hz), 7.44 (d, 4H, ^4J 1.5 Hz), and 7.57 (s, 12H); (**1d**) ($C_2D_2Cl_4$; 400 MHz): δ 1.32 (s, 36H), 7.07 (d, 2H, ^3J 16.5 Hz), 7.08 (s, 6H), 7.11 (d, 2H, ^3J 16.5 Hz), 7.30 (6H), and 7.48 (m, 16H).

expectation. However, the energetic gap increases strongly between the lowest and the highest charged state (Figure 2). In the case of the penta-anion it amounts to more than 1 V.

In the past twenty years the electrochemistry of conjugated phenylene–vinylene systems was studied mainly by Hörhold *et al.*[13] Describing the redox properties of these linear chain polymers they postulated the principle of effective conjugated segments (E.C.S.). This implies that a polymeric chain with a degree of polymerization m consists of x weakly interacting conjugated segments, each of which can be charged up to a di-ion state and contains k monomeric units ($1 < k \ll m, xk = m$). As the interaction energies between the segments are assumed to be low the redox potentials of the polymer should be determined only be the structure of the E.C.S. site. It is obvious that this concept resembles the bipolaron model.

Our electrochemical measurements suggest that the theoretical models of the redox behaviour of conjugated polymers must be amended. From an energy correlation diagram (Figure 2) constructed with our voltammetric data it can be deduced by extrapolation that the interaction energy between the charges in a dianion state decreased to a minimum only when the oligomeric chain contains at least eight monomeric phenyl–vinylene units ($n = 4$ corresponds approximately to 5.5 units). Furthermore, in solution no geometric stabilization effects of the charged species are observed.[14] This disagrees with the bipolaron model, which predicts a stabilized di-ion state within a chain segment of four monomeric units, but is in agreement with other electrochemical data which show that the charging of, *e.g.*, PPy up to 25 mol% occurs in a very small potential range. Hence, it follows that in a corresponding polymer with a degree of polymerization m, $m/4$ charges can be stored which interact only by spin pairing. As all these states are almost energetically degenerate only 'one' thermodynamic redox potential can be observed. In terms of the bipolaron model one bipolaron or spinless dianion state comprises a segment of eight monomeric units in the polymer.

However, as the experimental data also reveal, the polymer may in principle be charged up to almost 100 mol%, with the consequence that for charge numbers greater than $m/4$ the increasing Coulomb interactions gradually shift all the successive redox states to higher energies. In the limiting case of '$m - k$' charges ($k \ll m$) in the chain every further redox step will be energetically separated from the preceding one by at least the amount of the coulombic repulsion energy generated by the new charge. In practice, this upper limit is unavailable because degradation processes at such high potentials will destroy the material.

The results obtained may be useful for a better understanding of the charge storage mechanism in conventional conducting polymers such as PPy, PTh, and possibly even polyacetylene[6,15] in view of the fact that these systems also possess a chain-like conjugated structure similar to the oligo-*p*-phenylene–vinylenes studied.

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