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The oligomeric approach – the electrochemistry of conducting polymers in the light of recent research

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Abstract Electrochemical investigations on oligomeric model compounds (β-carotenoids) of polyacetylene varying the chain length in the range between 5 and 23 double bonds provide deeper insights into the redox properties of such systems. Furthermore, cyclic voltammetric studies of α,ω-diphenylpolyenes and phenylenevinylenes give clear evidence that the formation of the radical ions is followed by a rapid reversible dimerization between the oligomeric chains. The thermodynamic and kinetic parameters of the chemical reaction are presented. Applying these results to the properties of conducting polymers opens up new perspectives for interpreting charge storage and conductivity.

Key words Oligoene · Conducting polymers · Oligomeric approach · Cyclic voltammetry · Radical ions

Introduction

Although the physics and chemistry of conducting polymers have been studied for almost twenty years, a large number of phenomena are not well understood. On the one hand, this may be due to the fact that many of the experiments on these materials preferably yield general information rather than details of the molecular properties. On the other hand, theories and models borrowed from solid-state physics and macromolecular chemistry are often used to interpret the experimental data. One consequence of this practice is the application of the bipolaron model [1–8] to conducting polymers.

A promising solution to this problem lies in the study of the corresponding monodisperse oligomers with well-defined chemical structures. This allows one to monitor the chemical and physical properties systematically as a function of chain length and to extrapolate from them to the behaviour of the corresponding polymers.

Furthermore, spectroscopic data published in the literature in the past four years prove that, during charging, additional intermolecular interactions take place between charged conjugated oligomers [9–15]. For instance, UV/VIS and ESR spectra of the radical cations of some end-capped thiophenes [11–14], pyrrole [16] and aniline oligomers [17] are concentration- and temperature-dependent. In all cases, voltammetric analysis indicated the reversible formation of radical cations without chemical follow-up steps. Accordingly, it was concluded that weakly interacting π-mers formed rapidly and also decayed relatively quickly in the experimental time scale. Although the formation of π-mers would explain the rapid decrease in spin states during charging, this finding would not affect the underlying assumptions of the bipolaron model.

The "simplest" conjugated polymer is polyacetylene (PA). The discovery of its "metallic" properties by Heeger and McDiarmid [18, 19] at the end of the 70s stimulated worldwide efforts to develop new materials with unconventional properties. Although the stability of PA is poor, because of to the structural simplicity of its polyene chain it is still the subject of much basic research.

Despite the great interest in PA, there are only a few electrochemical studies of monodisperse oligoene systems. The reason is the high reactivity of doped alkyl-substituted oligoenes in the presence of nucleophiles or electrophiles. Normally, these oligomers consist of a carbon chain with alternating single and double bonds and two terminating groups R_1 and R_2, which are equal in most of the cases. Thus, a *tert*-butyl group [20–22] or, in the case of α- and β-carotenoids, a cyclohexene group [23, 24] have been used, while, in the so-called aryl-polyenes, phenyl or other aromatic substituents have been applied as end groups [25, 26].

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We present here the results of cyclic voltammetric studies of oligoenes. These investigations will give deeper insights to the intra- and intermolecular interactions between redox states. The correlation of these data with structural properties of oligomers provides information about their redox behaviour and that of the corresponding polymers.

Experimental

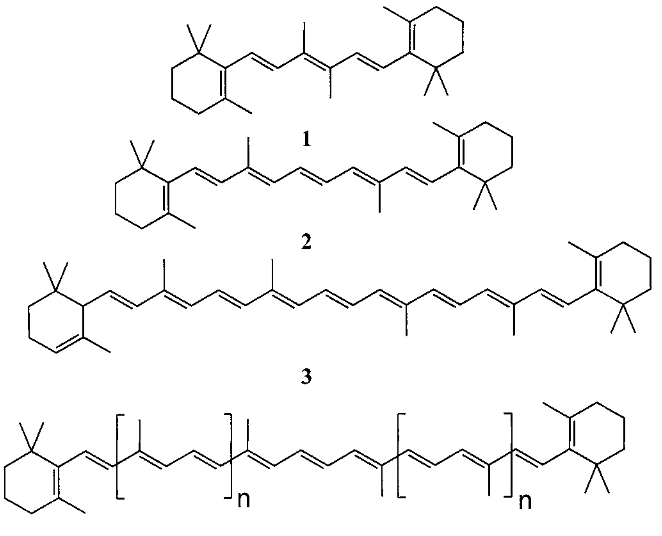
The experiments were performed using a three-electrode equipment with a platinum disk working electrode ($d = 1$ mm), a platinum counter electrode and an Ag/AgCl reference electrode (SO_2) or an Ag pseudo-reference electrode (dimethylamine), respectively. An EG&G Universal Programmer Model 175 and an Amel Model 553 Potentiostat were used, and data were recorded with an *xy* recorder or a transient recorder (K.R.E.N.Z. DSO).

Dimethylamine/tetrabutylammonium bromide (reduction) and sulfur dioxide/tetrabutylammonium hexafluorophosphate (oxidation) were used as solvent electrolyte systems. The purification of the solvents has been described elsewhere [27, 28].

Acetonitrile (HPLC grade, Fisons scientific equipment) was purified by distillation over calcium hydride. Methylene chloride (HPLC) was shaken with concentrated sulphuric acid several times and afterwards neutralized with sodium carbonate. It was then dried with calcium chloride and distilled over calcium hydride. The potentials were calibrated with the redox couples ferrocene/ferrocenium and cobaltocene/cobaltocenium (dimethylamine).

Results and discussion

In accordance with the findings on PA, the oligoenes **1**–**7** [29] can be both reduced and oxidized, which allows a simple electrochemical determination of the bandgap and the overall charge-storage properties of such systems. Cyclic voltammograms for the different species are shown in Figs. 1 and 2, and the apparent redox potentials are listed in Table 1.



n = 1: **4** n = 2: **5** n = 3: **6** n = 4: **7**

Formula 1

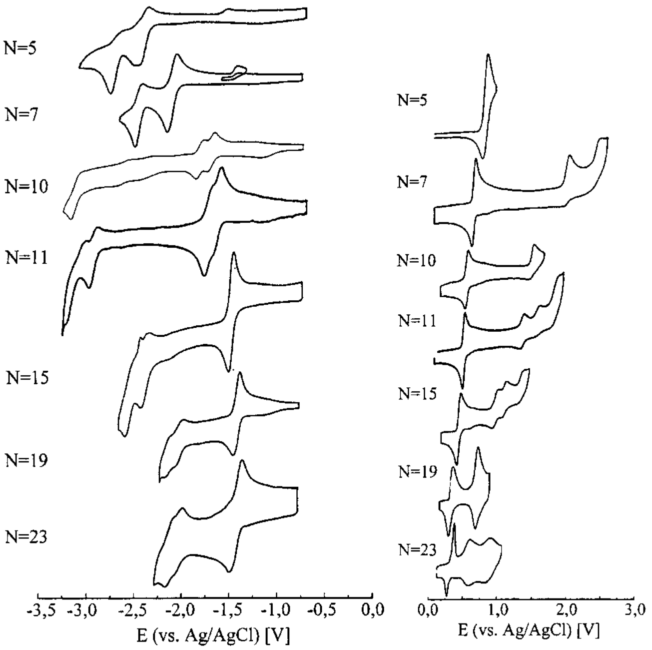


Fig. 1 Voltammograms of the reduction and oxidation of *β*-carotenoids (**1**–**7**) in dimethylamine/TBABr and $SO_2/TBAPF_6$. $T = 213$ K, $v = 0.1$ V/s

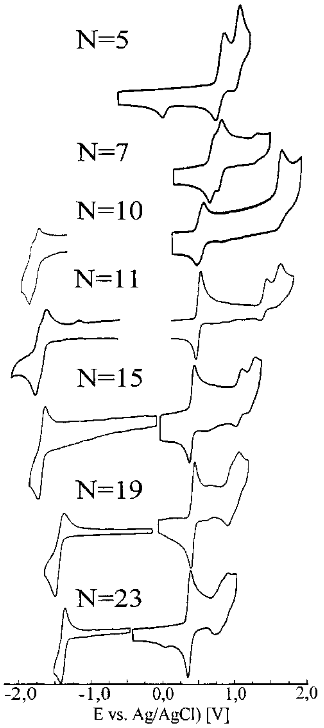


Fig. 2 Voltammograms of the reduction and oxidation of *β*-carotenoids (**1**–**7**) in $CH_2Cl_2/TBAPF_6$. $T = 213$ K, $v = 0.1$ V/s

As can be seen, the reduction for the system with $N = 5$ (N is the number of double bonds) starts with two

Table 1 Cyclic voltammetric data on **1**–**7**

Compound	N	Oxidation in SO_2^a				Reduction in DMA[a]			
		$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
1	5	0.82[b]		–	–	−2.36	−2.76[c]	–	–
2	7	0.67[b]		2.04[c]	–	−1.96	−2.27	–	–
3	10	0.56[b]		1.53[c]	–	−1.67	−1.81	−3.11	–
4	11	0.51[b]		1.35	1.54	−1.60	−1.69	−2.89	−3.08
5	15	0.43[b]		0.97	1.11	−1.47[b]		−2.42	−2.59[c]
6	19	0.33[b]		–	–	−1.39[b]		−1.99	−2.12
7	23	0.33[b]		–	–	−1.39[b]		−2.01	−2.11

[a] $E_{1/2}$ [V]; reference electrodes: Ag/AgCl-electrode (SO_2), Ag wire (DMA); $T = -60$ °C
[b] Two single-electron-transfer steps at the same potential
[c] Peak potentials

well-separated one-electron redox steps, while its oxidation in SO_2 already involves a two-electron transfer. However, the oxidation of the oligoenes in dichloromethane also starts with two separated one-electron redox steps, and, at a chain length equal to or greater than ten double bonds, the first oxidation wave involves two-electron transfer steps. Obviously, there is a strong influence of the solvent on the position of the redox potentials. With increasing chain length, further redox steps can be observed ($E_{\mathrm{Ox},3}$ and $E_{\mathrm{Ox},4}$ for oxidation, $E_{\mathrm{Red},3}$ and $E_{\mathrm{Red},4}$ for reduction). Similarly to the first two redox states, the potential separation between the third and the fourth redox step is small and decreases with increasing chain length. This is in close agreement with the simple HMO model which predicts that all two-electron states of one molecular orbital are energetically degenerated. The potential separation between these two redox states belonging to one MO results from the coulombic repulsion between such excess charges. Because the interaction between the charges of one MO disappears for longer oligoenes, several two-electron waves are observed for oligoenes with $N \geq 15$. In addition, the energetic separation between the two-electron pairs also decreases with increasing conjugation length.

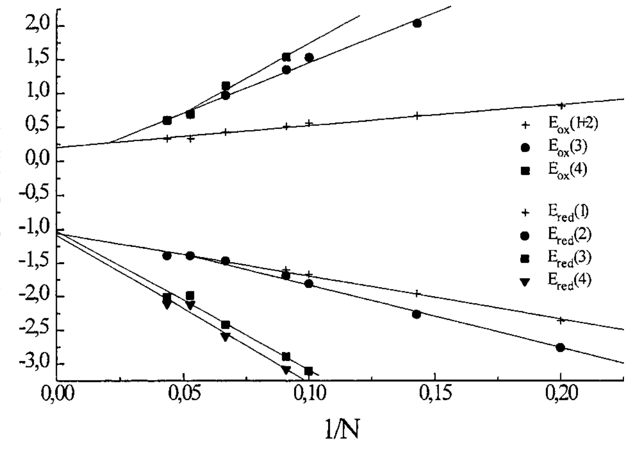


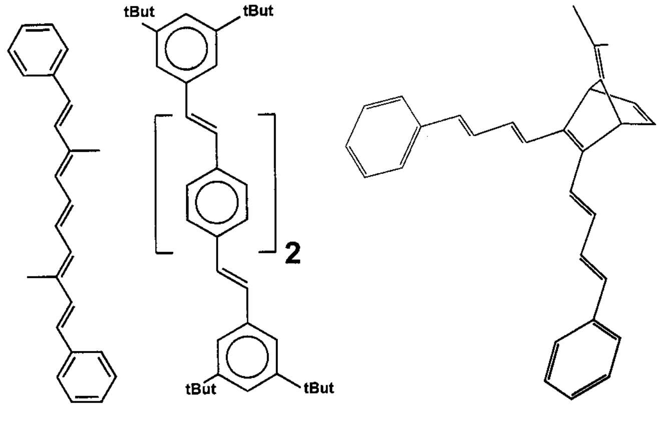
Fig. 3 Apparent redox potentials of **1**–**7** vs $1/N$ (N: number of double bonds). Dimethylamine/TBABr and SO_2/TBAPF$_6$, $T = 213$ K, $v = 0.1$ V/s

For all related redox states within the series, a strictly linear dependence of the redox potentials on the chain length of the oligomers is observed (Fig. 3). From the extrapolation of the first oxidation and reduction potentials plotted versus $1/N$, the bandgap for infinite long chains can be determined to be 1.25 eV, which is less than the experimental bandgap of PA [30]. It should be mentioned that so far no experimental proof for a strictly linear dependence of the redox potentials on $1/N$ are available for chain length longer than 23 double bonds. Furthermore, it is interesting to note that the potential separations between successive electron transfer steps are significantly higher in the case of reduction than in the case of oxidation. Obviously, specific ion pairing and solvent effects cause these differences.

From all these measurements the following trends can be established: With increasing chain length of an oligomer the conjugated π-system increases. This implies that:

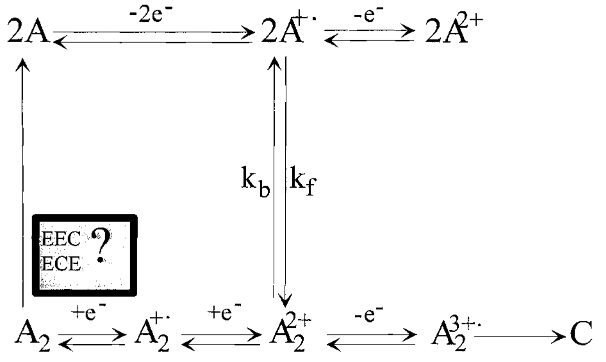
1. The number of possible redox states increases.
2. Redox states of identical charge (e.g. mono- or diion) shift towards lower energies (to more positive potentials upon n-doping and towards more negative potentials upon p-doping). For long chain lengths, the low redox potentials converge towards a limiting potential characteristic of the investigated conjugated polymer. Plots of E_1 versus the inverse chain length ($1/N$) show a linear dependence [31–33]. The limit $1/N = 0$ gives an estimate of the first redox potential of a hypothetical polymer consisting of infinitely long chains in solution (E_∞).
3. The potential difference between consecutive redox states decreases, because the coulombic repulsion between excess charges is reduced. At a certain chain length with about ten double bonds units, the potential difference between the first two redox states $\Delta E_{1,2}$ vanishes. In the past, this fact has often been interpreted as the minimum chain length for the formation of bipolarons.
4. The chemical stability of the charged species increases, and therefore the tendency for follow-up processes decreases. This is a consequence of rule 2.

The experimental data give no evidence of an extra stabilization of the diionic states as suggested by the



8 **9** **10**

Formula 2



Scheme 1

bipolaron model. It postulates that mainly the formation of bipolarons (diions) causes an intramolecular distortion in the chain-like conjugated systems, resulting in a flattened chain structure [1–8].

Recently, cyclic voltammetric studies of the oxidation of diphenylpolyenes **8**, **9** [34] and **10** have indicated strong changes of the voltammetric response as a function of temperature, concentration and scan rate. A detailed evaluation of all data gave clear evidence that the formation of the radical ions is followed by a rapid reversible dimerization between oligomer chains accompanied by the formation of a σ-bond.

Already, a qualitative analysis of these results indicates a reversible follow-up reaction. At low scan rates ($v = 0.1\ \mathrm{V \cdot s^{-1}}$), the follow-up reaction linked to the charge transfer achieves thermodynamic equilibrium (Fig. 4). In other words, the radical cation produced at the electrode undergoes a fast dimerization in the time scale of the experiment. Concurrently, the dimer reacts at a lower backward rate to again form the radical cation, which then can be reduced to its neutral species. As a consequence, in the voltammetric experiment, a reversible redox process is observed. As the scan rate increases, the influence of the slow reverse reaction diminishes, and the radical cation ceases to be regenerated in the experimental time scale. Consistent with this, in the voltammetric experiment, the signal for the reduction of the radical cation diminishes, and a new cathodic wave for the reduction of the follow-up product appears. Finally, at high scan rates, the time scale becomes so short that the radical cation no longer reacts within it, and in the cyclic voltammogram the waves of the $A/A^{+\cdot}$ and $A^{+\cdot}/A^{2+}$ pairs approach those of pure redox processes.

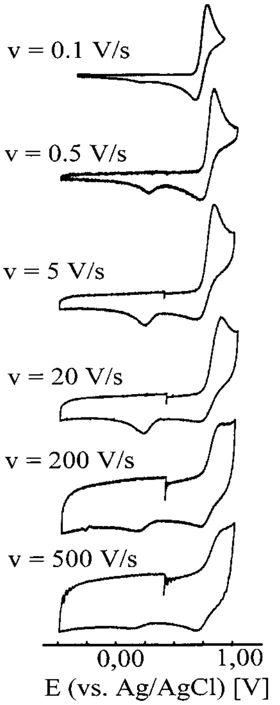


Fig. 4 CV of **9**, different scan rates. $T = 253$ K, CH_2Cl_2

The high concentration dependence of voltammetric signals leads to the conclusion that the charge transfer is followed by a second-order reaction, and that this reaction is a dimerization process (Fig. 5). Raising the concentration of the redox-active species increases the

Table 2 Formal redox potentials of **8**, **9** and **10**; $T = 273$ K; $v = 0.1\ \mathrm{V \cdot s^{-1}}$

	8[a]	**9**[a]	**9**[b]	**10**[a]	
E_1 Monomer	[V]	0.72	0.59	0.61	1.00
E_2 Monomer	[V]	0.98	1.00	0.98	1.26
$E_{1\ \mathrm{Peak}}$ Dimer	[V]	0.18–0.24	≈0.26	≈0.24	0.5–0.9
$E_{2\ \mathrm{Peak}}$ Dimer	[V]	0.18–0.24	≈0.26	≈0.24	0.5–0.9
$E_{3\ \mathrm{Peak}}$ Dimer	[V]	1.8	–	–	–

[a] CH_2Cl_2
[b] Acetonitrile (ACN)

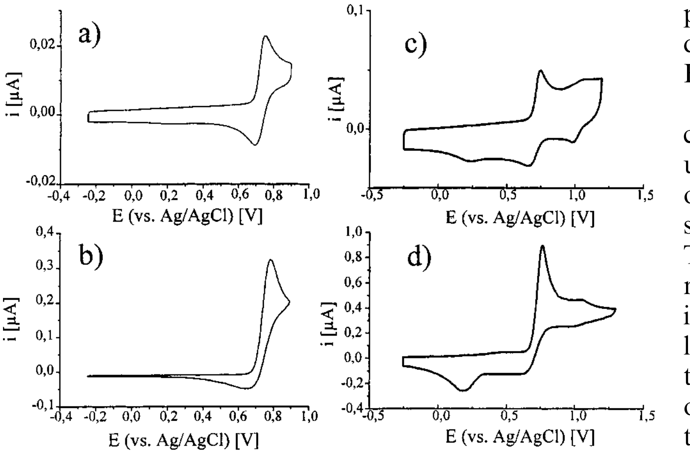


Fig. 5a–d CV of **8**, concentration dependence: **a** and **c** $c = 5 \cdot 10^{-5}$ M, **b** and **d** $c = 9.9 \cdot 10^{-4}$ M. $T = 233$ K; **a** and **b** $v = 0.02$ V/s, **c** and **d** $v = 0.1$ V/s

rate of the coupling reaction between the radical ions without affecting the kinetics of the first-order reverse reaction. The transition from a thermodynamically to a kinetically controlled reaction determines, in turn, that the dimerization reaction dominates. In the cyclic voltammogram, the waves signalling the reduction of the radical cation or its oxidation to the dication diminish or even disappear completely.

The experimental results obtained by lowering the temperature confirm the mechanism proposed for room temperature conditions (Fig. 6). Owing to negative reaction enthalpy and the fading influence of reaction entropy, the equilibrium shifts towards the dimeric dication as the temperature decreases. The reaction rate therefore slows down and the species decays. As a result, the reaction is kinetically controlled even at low scan rates, and, in the voltammetric reverse scan, the signal for the reduction of the dimeric follow-up product is particularly strong. So far, it has not been possible to determine whether this reduction process follows an EEC or an ECE mechanism.

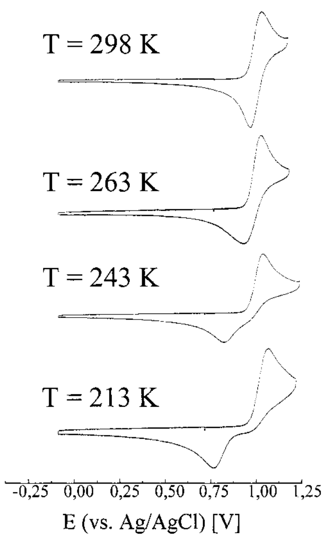


Fig. 6 CV of **10** at different temperatures; $v = 0.1$ V/s, CH_2Cl_2

Quantitative evaluation of the voltammetric data confirms the qualitative picture. The rate and equilibrium constants of the chemical reaction of **8** and **9** were obtained from working curves [35][1] (Fig. 7) and digital simulations [36–38], and the results are summarized in Tables 3 and 4. Using the voltammetric data of **10**, a rough estimate of the rate and equilibrium constants, including their temperature dependence, results in similar values. The analysis provides unequivocal proof of the dimerization of radical cations (RR coupling), not as often postulated for irreversible processes in the literature a coupling between neutral species and radical cations (RS coupling) [39, 40].

Particularly striking is the low temperature dependence of the rate constants for the dimerization. As a result, the values of the activation enthalpy are close to zero or even negative. Reactions involving apparently negative activation energies have already been described in the literature [41–46]. To interpret them, one assumes a rapid initial equilibrium reaction with a negative standard reaction enthalpy larger than the activation energy of the dimerization itself [41, 42]. In the current case, though, it is unclear which process could make a sufficiently large negative contribution. Diffusion-controlled processes between similarly charged particles can also cause relatively low rate constants despite low activation parameters as have been measured a number of times for dimerization reactions of radical ions [43–46].

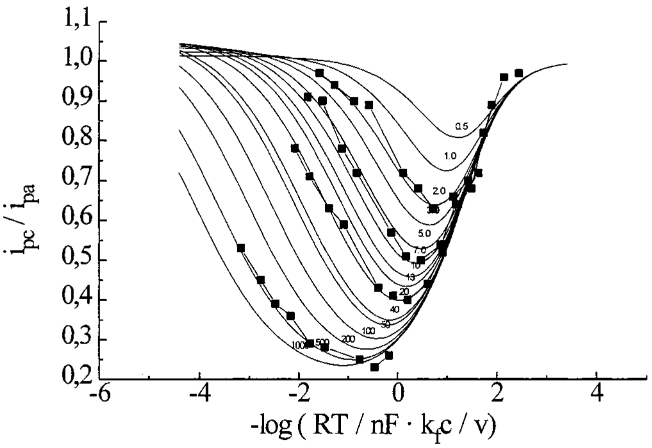


Fig. 7 Experimental i_{pc}/i_{pa} values in dependence on scan rates v (—■—) and working curves (————) for reversible dimerization

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[1] Digital simulations were used to obtain the working curves for a reversible dimerization reaction. The application of electrodes with different radii caused problems in evaluation, because it was not possible to take into account the influence of the electrode size on the resulting diffusion field (e.g. hemispherical mass transport) and, thus, on the shape and size of the voltammetric signal. Therefore, the rate constants and the activation parameters have an of error of at least ±20%

Table 3 Rate and equilibrium constants for the reversible dimerization

	T = 298 K	T = 273 K	T = 253 K	T = 233 K
8[a]				
K [l mol^{-1}]	$1 \cdot 10^4$	$6 \cdot 10^4$	$1 \cdot 10^5$	$2 \cdot 10^6$
k_f [l mol^{-1} s^{-1}]	$5 \cdot 10^6$	$5 \cdot 10^6$	$5 \cdot 10^6$	$5 \cdot 10^6$
k_b [s^{-1}]	500	85	33	2.5
9[a]				
K [l mol^{-1}]	$1.2 \cdot 10^5$	$1.2 \cdot 10^6$	$1 \cdot 10^7$	$3 \cdot 10^8$
k_f [l mol^{-1} s^{-1}]	$5 \cdot 10^6$	$5 \cdot 10^6$	$5 \cdot 10^6$	$5 \cdot 10^6$
k_b [s^{-1}]	42	4.2	0.5	0.02
9[b]				
K [l mol^{-1}]	$3.5 \cdot 10^{5}$[c]	$3.45 \cdot 10^6$	$8.64 \cdot 10^7$	–
k_f [l mol^{-1}s^{-1}]	$3 \cdot 10^{6}$[c]	$3 \cdot 10^6$	$3 \cdot 10^6$	–
k_b [s^{-1}]	9[c]	0.9	0.04	–

[a] CH_2Cl_2
[b] Acetonitrile (ACN)
[c] T = 293 K

Table 4 Reaction[a] and activation[b] parameters of the reversible dimerization

	8[c]	**9**[c]	**9**[d]
ΔH^0 [kJ mol^{-1}]	−46	−69	−85
ΔS [J mol^{-1} K^{-1}]	−80	−133	−124
$\Delta H^{\#}_{f}$ [kJ mol^{-1}]	−2.2	−2.2	−2.3
$\Delta S^{\#}_{f}$ [J mol^{-1} K^{-1}]	−124	−124	−128
$\Delta H^{\#}_{b}$ [kJ mol^{-1}]	44	67	83
$\Delta S^{\#}_{b}$ [J mol^{-1} K^{-1}]	−44	11	57

Measurements using
[a] van't Hoff reaction isobars
[b] Eyring-plot
[c] CH_2Cl_2
[d] ACN

One can obtain quantitative results using the Debye-Smulochowski theory [47]. However, further theoretical and experimental work is needed to clarify details of the elementary steps.

So far, all reports of intermolecular reactions between radical cations of conjugated systems postulate the formation of π-mers. The distance dependence of the bonding interactions in the cases of Wursters blue [48] and viologens [49] may indicate the existence of such complexes. Moreover, the lack of any electrochemical evidence of a follow-up reaction was interpreted as a rapid equilibrium reaction with low reaction energies.

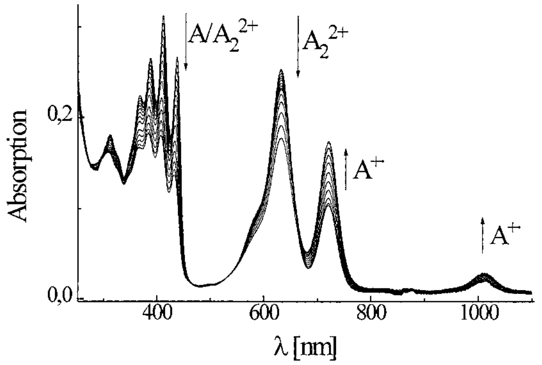

Fig. 8 Absorption spectra of $\mathbf{8}^{+\cdot}$ and its dimer; temperature varies from $T = 233$ K to $T = 273$ K, CH_2Cl_2, oxidant: $FeCl_3$

On the other hand, in most cases the charge-transfer bands one would expect were not observed in the UV/VIS spectra of the radical cations either of oligomeric thiophenes or pyrroles [50]. To explain this, it was assumed that π-mers are not easily polarizable [16]. Nor did we find any charge-transfer bands in the UV/VIS spectra of the radical cations of **8** and **9** (Fig. 8). Rather, the bands, which can be associated to the dimer, all have shorter wave lengths than the monomer. The very large reaction enthalpies [34] (not bonding enthalpies) of between −60 and −90 kJ · mol^{-1} for the formation of the dimers, the very similar rate constants of **8**, **9** and **10** despite differences in steric hindrance, and the continued coulombic repulsion together speak against a simple charge-transfer interaction. Although the coulombic repulsion in the gas phase is fully effective, AM1 calculations, assuming a benzylic σ-bond between two charged monomer chains of **8**, indicate that such a system is about 167 kJ · mol^{-1} more stable than the pure complex.

In the case of 4,4′-dimethoxystilbene, the smallest unit of the structurally related diphenylpolyenes and phenylenevinylenes, whose radical cations also undergo reversible dimerization in a benzylic position[2], the product of coupling after the addition of water could be isolated as a derivative of tetrahydrofurane [51] (J. Heinze, H.J Schäfer, P. Hauser, unpublished results). Effenberger's studies of dimeric σ-complexes of 2,4,6-tripyrrolidinobenzene derivatives also indicate a dimerization of radical cations [52, 53].

All these findings lead one to conclude that a σ-bond forms between the two charged monomers, analogous to the reversible dimerization of radical anions [43–46, 54–56]. The possible formation of σ-bonds between radical cations of oligomeric thiophene derivatives has also attracted the interest of other authors [57].

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[2] In ultradry CH_2Cl_2 or ACN, two apparently reversible redox processes take place, forming a dication. Analogous voltammetric findings were obtained by variation of temperature, concentration and scan rate

The number of oligomeric systems known to exhibit this behaviour has risen substantially in the meantime. Besides oligoenes, oligomeric thiophenes [58], substituted *p*-benzoquinones [59] (J. Heinze, P. Hauser, unpublished results) and 2,3,7,8-tetramethoxythianthrene [60] also dimerize. Very recently, high-resolution ^{13}C-NMR investigations have proved the reversible dimerization of C_{60} radical anions by the formation of a σ-bond between two C_{60} units [61]. In the case of anthracene-9-carboxylate radical anions [62] and polyene radical dications [63], the reversible formation of σ-bonds was proved by ^{1}H-NMR spectroscopy. Such processes have been postulated in the literature several times [64–66]. It appears that a general reaction principle for radical (cat)ions has been discovered. So far, most of the experimental evidence comes from conjugated chain-like oligomers. The respective structure of the system and environmental influences determine the equilibrium and kinetics of such reactions.

Conclusions

Applying these results to the properties of conducting polymers opens up new perspectives for interpreting charge storage and conductivity. Contrary to the predictions of the bipolaron model, the energetic stabilization of such systems does not depend on lattice relaxation subsequent to distortion of the geometry of the chain segment by a polaron or bipolaron. It is the result of the intermolecular coupling of two π-radical centres to form a σ-bond. In the case of polymers, this produces a network. As experiments prove, the latter process produces a marked stabilization and, in addition, results in localized charges. This explains the marked hysteresis between charging and discharging and the low conductivity at low charging levels [67].

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